

MORPHOLOGICAL AND STRUCTURAL CRYSTALLOGRAPHY AND OPTICAL PROPERTIES OF SILICON CARBIDE

BY

NEWMAN W. THIBAUT

CONDENSED FROM A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN, FEBRUARY, 1943

Reprinted from *American Mineralogist*, 29, 249-278 and 327-362 (1944)



MORPHOLOGICAL AND STRUCTURAL CRYSTALLOGRAPHY AND OPTICAL PROPERTIES OF SILICON CARBIDE (SiC)*

PART I: MORPHOLOGICAL CRYSTALLOGRAPHY AND ETCHING FIGURES

NEWMAN W. THIBAUT,
Norton Company, Worcester, Massachusetts.

TABLE OF CONTENTS

Introduction.....	250
Acknowledgments.....	250
Morphological Crystallography.....	251
Review of Literature.....	251
Alpha SiC.....	254
Introduction.....	254
Type I.....	254
Type II.....	256
Type III.....	261
Type IV.....	261
Type V.....	262
Type VI.....	265
Relationship of Types.....	266
Coalescence of Types.....	267
Twinning.....	269
Beta SiC.....	270
Etching Figures.....	274
Review of Literature.....	274
Etchings by Fusion Methods.....	275
Etchings by Chlorine.....	277

ABSTRACT

The morphological crystallography of β -SiC (cubic), and of five modifications or "types" of α -SiC (hexagonal), two of them new, is given in detail. Each of the α -SiC types is characterized by its own series of crystal forms, those of types I, IV and VI being typical for crystals based on rhombohedral lattices, while those of types II and III are characteristic of hexagonal lattices. Each α -SiC type must be referred to its own axial ratio, all of which, however, are rationally related, and the crystal forms common to two or more of the types are those whose indices are equivalent when referred to the greatest common divisor axial ratio. Two or more of the hexagonal modifications often coalesce in such a

* Condensed from a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, February, 1943.

manner that c and a axes are common and the basal pinacoids form the plane of contact. Two methods of twinning were noted. In the more common case it was impossible to distinguish between two possible laws: twinning axis perpendicular to a common first order pyramid, or twinning plane parallel to a very rare first order pyramid. The second twinning arrangement, involving only type I crystals, obeys the law: twinning axis, the c axis. Crystal measurements made on β -SiC for the first time indicate the hextetrahedral class of the isometric system. Beta SiC is commonly intergrown with α -SiC in such a manner that tetrahedron faces of the former are in contact with or parallel to basal pinacoids of the latter.

Etching figures obtained on crystals of the α -SiC types by the use of Cl_2 at 1000°C . and by fused borax indicate that α -SiC, types I, IV and VI are ditrigonal-pyramidal, and that types II and III are dihexagonal-pyramidal. Etching phenomena reveal that purely morphological criteria are inadequate for the distinction between upper and lower basal pinacoids.

INTRODUCTION

Many studies have been made of the morphology and structure of silicon carbide, and of its physical properties, including density and indices of refraction, but there has been no attempt to correlate the data for the many observed modifications, nor to seek the relationships among them. Moreover, in addition to the lack of consistency and the incompleteness of the literature on the subject, little work has been done on crystals of known chemical analysis. For these reasons it seemed advisable to undertake a detailed study of the morphological and structural crystallography, and the optical constants of this substance.

The investigation has been carried out in the Laboratories of Norton Company, with the exception of the x -ray determinations which were made in the Mineralogical Laboratory at the University of Michigan. Although silicon carbide manufactured by the Norton Company under the trade name "crystolon" supplied most of the material for the study, commercial SiC manufactured by all the American and most of the important foreign producers was included.

ACKNOWLEDGMENTS

The writer greatly appreciates the co-operation extended him by the many concerns which supplied material for examination. In this respect particular thanks are due the Lonza Electric and Chemical Works, Ltd., Basel, Switzerland.

The author is indebted to Mr. A. A. Klein and other members of the Norton Laboratories both at Worcester, Massachusetts, and Chippawa, Ontario, for their counsel throughout the study, and to Norton Company which made the investigation possible and assisted financially in the publication of the results; to Professor L. S. Ramsdell and the other members of the staff of the Mineralogical Laboratory, University of Michigan, for their advice and assistance in the execution of the study. Aid in specific problems is acknowledged in the text.

MORPHOLOGICAL CRYSTALLOGRAPHY

REVIEW OF LITERATURE

Frazier (1893) examined platy crystals of SiC, the yellow-green of which showed a distinct rhombohedral-like development while the blue were apparently hexagonal holohedral. The axial ratio and most of the crystal forms observed by Frazier as well as by subsequent investigators are contained in Table 1, while forms which must be considered uncertain are listed in Table 2. The one twin observed was said to obey the law: twinning plane, the unit rhombohedron (now designated by the letter r).

Becke (1895) studied poorly developed tabular crystals. He also described twins similar to that observed by Frazier, but recognized two possible laws: (1) twinning axis normal to the unit trigonal pyramid (now designated r), or (2) twinning plane the form $(10\bar{1}4)$ (now represented by E). Becke believed the first possibility to be more likely since it is a more common twinning law.

Negri (1902) measured almost a hundred SiC crystals, some of which were apparently hexagonal holohedral, while others appeared to be rhombohedral. He, however, referred them all to the hexagonal-scalenohedral class. A later investigation which was to have included the results of etching experiments, and a discussion of 22 other rare and very rare forms was unfortunately never published.*

Baumhauer (1912), studying 20 small tabular SiC crystals, divided them into three groups, or "types," each having its own characteristic suite of forms, but referred them all to the same axial ratio. Some forms were common to two types, but only the base was common to all three. Crystals of the first type clearly showed a rhombohedral-like development and were considered hexagonal-scalenohedral, while those of types II and III were apparently holohedral and said to be dihexagonal-dipyramidal. Crystals of the different types were adjacent to and irregularly intergrown with one another, and in two cases there was a coalescence of types I and II in such a manner that, although each crystal was apparently single and homogeneous, all the faces adjacent to one base were those of type I while all faces adjacent to the other base belonged to type II. The plane of contact between the two types was parallel to both basal pinacoids. The yellow crystals were found to be type I, the green, type II, while all three types were represented by the dark blue and black SiC.

Baumhauer (1915) described additional cases of coalescences of the SiC

* Personal communication from Professor A. Pelloux, Director, Institute di Mineralogia, Genoa, Italy, August 26, 1939.

types. Evidence for hemimorphism was afforded by the distribution of iridescent coatings on the various crystal faces, so Baumhauer considered type I ditrigonal-pyramidal. Certain triangular markings discussed more fully later led him to conclude that type II also belonged to the same class. Type III was considered dihexagonal-pyramidal. Two modes of twinning were reported: twinning plane the first order prism, and twinning plane the basal pinacoid.

Weigel (1916) observed many crystals of hexagonal SiC whose twinning plane was said to be that of a pyramid.

Espig (1921) confirmed Baumhauer's observations of SiC types and coalescences, and twinning parallel to the base. Crystals of type I were said to be yellow-green, while those of type II were blue.

The crystal of cubic SiC studied by Braekken (1930) was reported to be octahedral with poor skeletal faces, but apparently no goniometric measurements were attempted.

Peacock and Schroeder (1934) studied thin tabular crystals all of which proved to be type II. The indices of the forms of all the known SiC types were simplified to the greatest possible extent by referring each type to its own individual axial ratio, namely, that resulting from the *x*-ray studies of Ott (1925*a*, 1925*b*, 1926).

Appended to the above article, Peacock (1934) has described SiC crystals in the collection at Harvard University. The forms listed in Table 1 under type I were observed.

Cortelezzi and Schroeder (1934) studied type II crystals, some or all of which were apparently the same as those studied by Peacock and Schroeder.

The Handbook of Chemistry and Physics (1943) and Wyckoff (1931) refer to the three modifications of SiC mentioned above as SiC I, II and III. Cubic SiC is designated SiC IV, and the hexagonal modification with 51 formula weights per cell as described by Ott (1928) is noted as SiC V.

Table 1, which correlates the crystal forms observed by the different authors, is divided by heavy vertical lines into four major sections. The earlier investigators referred all crystals to the same *c*:*a* ratio, but did not distinguish definite crystal types. Later Baumhauer and Espig each recognized three definite types but referred all to an axial ratio twice that of the earlier writers. Peacock and Schroeder, Peacock, and Cortelezzi and Schroeder recognized the three types but referred each to its own unique axial ratio. Finally, the present writer has distinguished five crystal types each with its own *c* value and has for the first time definitely differentiated between upper and lower forms by etching methods.

There is some doubt as to the number of types observed by the early investigators and the proper correlation of forms later found to be com-

Digitized by the Internet Archive
in 2026

TABLE 2. UNCERTAIN FORMS ON α -SiC

Angle to Base		Letter	Symbol	(when) $c =$	Observed by	α -SiC type	Times Observed
Observed	Calculated						
?	15°49'*	—	1/5	1.2264	Frazier (1893)	?	?
?	81°32 $\frac{1}{2}$ '*	—	19/4	1.2264	Frazier (1893)	?	?
35°20'	35°18 $\frac{1}{2}$ '	E^{**}	(10 $\bar{1}$ 4)	2.4532	{Baumhauer (1915)	I	1
					{Espig (1921)	?	1
43°20 $\frac{1}{2}$ '	43°21 $\frac{1}{2}$ '	—	(10 $\bar{1}$ 3)	2.4532	Baumhauer (1915)	III	1
?	57°34 $\frac{1}{2}$ '*	—	{(50 $\bar{5}$ 9)}	2.4538	Espig (1921)	?	2
			{(50 $\bar{5}$ 9)}				
?	87°58 $\frac{1}{2}$ '*	—	(10 . 0 . 10 . 1)	2.4538	Espig (1921)	I?	1
84°55'	84°57 $\frac{1}{2}$ '	—	(20 $\bar{2}$ 1)	4.9070	Thibault	II	1
70°29'	70°33 $\frac{1}{2}$ '	x	(10 $\bar{1}$ 7)	17.174 ₆	Thibault	IV	1
50°16 $\frac{1}{2}$ '	50°09 $\frac{1}{2}$ '	$\bar{D}$	(0 . 1 . 1 . 26)	26.989	Thibault	VI	1
48°24'	48°03 $\frac{1}{2}$ '	$\bar{C}$	(1 . 0 . 1 . 28)	26.989	Thibault	VI	1
54°49'	54°47'	$\bar{F}$	(1 . 0 . 1 . 22)	26.989	Thibault	VI	1

* Calculated from symbols and axial ratios given by the authors.

** Letter assigned by the writer to facilitate reference to the form in connection with twinning.

mon to two types. This is indicated by question marks in Table 1. Except in one case Espig gave no observed angles for the forms which he listed, and, from the data which he presented, the writer was not able to gain a clear conception of the combination of forms or types on many of the crystals which he described. For example, although the indices given for several forms would indicate that Espig observed faces belonging to the new modification now designated α -SiC, type IV, these faces did not always occur in the proper sequence and faces of forms belonging to other hexagonal SiC modifications were interspersed in an irregular manner. The same may be said of (11.0. $\bar{1}$ 1.5) which is equivalent to one of the forms of the new modification, type VI. Espig apparently recognized only modifications I, II and III, and did not explain the presence of these faces which did not belong to the simple arithmetical series of forms of the first three types. Although these forms might be considered questionable, they are included in Table 1 for the purpose of correlation with equivalent forms now definitely established.

ALPHA SiC

Introduction. Commercial abrasive silicon carbide consists very largely of hexagonal or α -SiC crystals in all states of perfection, intergrowths and aggregates of subhedral crystals and dense crystalline masses. Usually small amounts of cubic or β -SiC and certain impurities are also present.

Euhedral crystals are most frequently tabular parallel to the base. In such a case one basal pinacoid is usually well developed while the other is poorly developed or absent altogether, but this is not universal. Less commonly the individuals are thick tabular to equant, and rarely, elongated parallel to the c axis. Crystals showing skeletal growth with prisms and pyramids accompanied by many horizontal striae and re-entrant angles are very common.

About a hundred and fifty crystals were completely measured during the course of this study, and, in addition, certain zones on about five hundred more were investigated. A one-circle goniometer was used almost exclusively.

Type I. This type is apparently the second most common of the α -SiC modifications. As indicated by Tables 3 and 4, and Fig. 1, the crystals are rhombohedral-like in development as evidenced by the different series of forms characteristic of alternate first order trigonal pyramid zones. One very small black crystal contained five faces of the new form $\bar{b}$. In this case, as well as with individuals of types II and III and 24 minute crystals of undetermined type examined under the stereoscopic microscope, all faces of the second order pyramid occurred adjacent to only one of the basal pinacoids which etching showed to be the lower form.

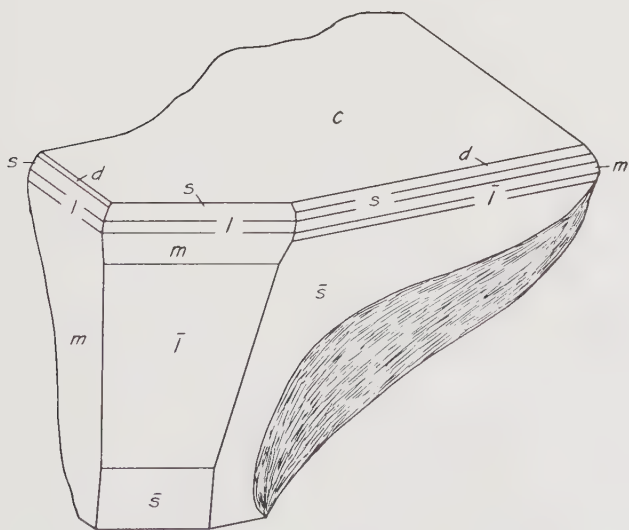
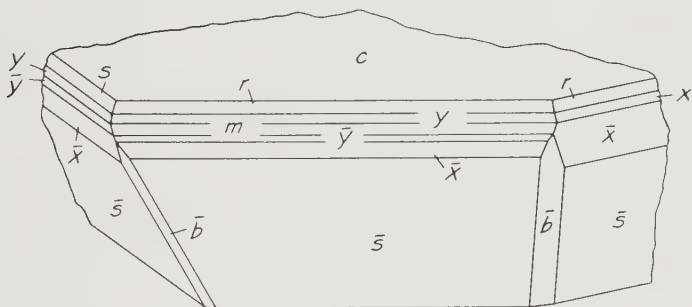
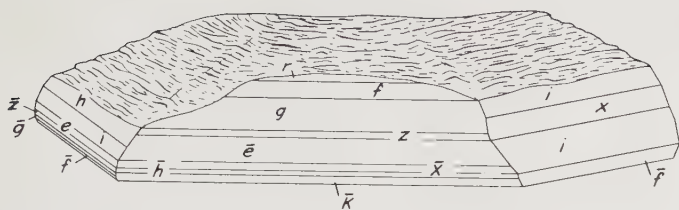


FIG. 1 (top). Alpha (hexagonal) SiC, type I.

FIG. 2 (center). Alpha SiC, type II, showing new second order pyramid, $\bar{b}$.

FIG. 3 (bottom). Alpha SiC, type III.

As will be discussed in the section devoted to etching figures, type I SiC is hemimorphic, belonging to the ditrigonal-pyramidal class of the hexagonal system. Previous investigators apparently distinguished between upper and lower forms from a consideration of the crystal habit. For example, Becke (1895) retained the larger and more perfectly developed base as the upper form and stated that the lower trigonal pyramids were larger and more numerous, while Peacock (1934) spoke of hemimorphism as evident in the very poor development of the lower trigonal pyramids.

The present study of a larger number of crystals has indicated that morphological criteria for the distinction between upper and lower forms are inadequate. While as a whole the upper first order pyramids, especially those least inclined to the basal pinacoid, were found to be more numerous than the corresponding lower forms, and the upper basal pinacoid larger and more perfectly developed than the lower, several individual crystals violated these generalizations. Thus etching experiments, or possible electrical tests such as for pyroelectricity, are necessary for the reliable distinction between upper and lower forms, and, since it does not appear that any of the previous investigators used such methods for separating these forms, it seems likely that their distinctions between them as indicated in Table 1 were often incorrect, except when faces of both upper and corresponding lower forms occurred on the same crystal. In the present work all distinctions have been made on the basis of differential etching of the basal pinacoids. Form $\bar{b}$ is probably good morphological evidence of hemimorphism, but this form is only present very rarely.

Table 3 contains the morphological data for type I. The axial ratio on which the calculated values and indices are based is that which is indicated by the x -ray study, and gives the greatest simplification of the form indices. Within the limits of error of the measurements, it was found to be rationally related to the very precisely determined $c:a$ value of type II crystals by a factor of $2\frac{1}{2}$, as indicated in Table 8. Table 4 contains an angle table for two-circle goniometry. Insofar as possible, the presentation of the crystallographic data follows the procedure adopted for the new edition of Dana's *System of Mineralogy* as outlined by Wolfe (1941).

Type II. As observed by the previous investigators, crystals of type II were found to be by far the most abundant. The type has been studied in greater detail and the axial ratio more precisely determined than is true of the other types, and it therefore serves as a standard of comparison.

Table 5 gives the morphological data for type II crystals as determined on the one-circle goniometer. Partial data from two-circle measurements

TABLE 3. MORPHOLOGICAL DATA, TYPE I SiC

Form	No. Times Observed	Quality	Angle between Form and Base		
			Measured Range	Weighted Average	Calculated Value
$c\text{-}\bar{c}$	0001	22	A-C	—	0°00'
M	1.0. $\bar{1}$.13	1	C	47°30'	47°27 $\frac{1}{2}$ '
r	1.0. $\bar{1}$.10	2	A-B	54°46'	54°47'
$f\text{-}\bar{f}$	10 $\bar{1}$ 7	13	A-C	63°37' - 63°45'	63°42 $\frac{1}{2}$ '
$g\text{-}\bar{g}$	10 $\bar{1}$ 4	7	A-C	74°11' - 74°19'	74°14 $\frac{1}{2}$ '
$z\text{-}\bar{z}$	10 $\bar{1}$ 1	9	A-C	85°51' - 86°02'	85°57 $\frac{1}{2}$ '
$\bar{k}$	0.1. $\bar{1}$.14	1	C	45°10'	45°20'
$h\text{-}\bar{h}$	0.1. $\bar{1}$.11	5	B-C	52°10' - 52°13'	52°11'
$i\text{-}\bar{i}$	01 $\bar{1}$ 8	12	A-C	60°30' - 60°40'	60°33'
$x\text{-}\bar{x}$	01 $\bar{1}$ 5	6	A-C	70°30 $\frac{1}{2}$ ' - 70°35'	70°33 $\frac{1}{2}$ '
$e\text{-}\bar{e}$	01 $\bar{1}$ 2	5	B-C	81°52' - 82°00'	81°56'
$\bar{b}$	1.1.2.15	5	D-E	58°32 $\frac{1}{2}$ ' - 58°36 $\frac{1}{2}$ '	58°34 $\frac{1}{2}$ '

TABLE 4. α -SiC, TYPE I, ANGLE TABLEHexagonal— R ; ditrigonal pyramidal— $3m$

$$a:c = 1:12.267_5$$

$$p_0:r_0 = 14.165_3:1$$

$$\alpha = 13^\circ 54\frac{1}{2}'$$

$$\lambda = 119^\circ 30\frac{1}{2}'$$

Lower	Upper		ϕ	ρ	A_1	A_2
$\bar{c}$	c	0001	—	0°00'	90°00'	90°00'
	M	1.0. $\bar{1}$.13	+30°00'	47°27 $\frac{1}{2}$ '	50°21'	90°00'
	r	1.0. $\bar{1}$.10	+30°00'	54°47'	44°58'	90°00'
$\bar{f}$	f	10 $\bar{1}$ 7	+30°00'	63°42'	39°04'	90°00'
$\bar{g}$	g	10 $\bar{1}$ 4	+30°00'	74°14'	33°33'	90°00'
$\bar{z}$	z	10 $\bar{1}$ 1	+30°00'	85°57 $\frac{1}{2}$ '	30°15'	90°00'
$\bar{k}$		0.1. $\bar{1}$.14	-30°00'	45°20'	90°00'	51°59'
$\bar{h}$	h	0.1. $\bar{1}$.11	-30°00'	52°10'	90°00'	46°50 $\frac{1}{2}$ '
$\bar{i}$	i	01 $\bar{1}$ 8	-30°00'	60°32 $\frac{1}{2}$ '	90°00'	41°03 $\frac{1}{2}$ '
$\bar{x}$	x	01 $\bar{1}$ 5	-30°00'	70°33 $\frac{1}{2}$ '	90°00'	35°15'
$\bar{e}$	e	01 $\bar{1}$ 2	-30°00'	81°58'	90°00'	30°57 $\frac{1}{2}$ '
$\bar{b}$		1.1.2.15	0°00'	58°33 $\frac{1}{2}$ '	64°45'	64°45'

on two crystals showing form $\bar{b}$, one of which is illustrated by Fig. 2, are included in Table 6. This shows that $\bar{b}$ is a second order pyramid since the ϕ value is 30° from that of the other pyramids which were found to be first order forms.

TABLE 5. MORPHOLOGICAL DATA
TYPE II SiC

Form	No. Times Ob- served	Qual- ity	Angle between Form and Base		
			Measured Range	Weighted Average	Calcu- lated Values
$c-\bar{c}$ 0001	67	A-B	—	—	0°00'
m 1010	26	A-B	89°56' -90°01½'	90°00'	90°00'
$n-\bar{n}$ 1015	23	C-D	48°27' -48°40½'	48°33½'	48°34½'
$r-\bar{r}$ 1014	17	A-B	54°45' -54°53'	54°47'	54°47'
$s-\bar{s}$ 1013	56	A-B	62°03' -62°08'	62°06'	62°06'
$x-\bar{x}$ 1012	34	A-B	70°29½' -70°35½'	70°33½'	70°33½'
$y-\bar{y}$ 1011	31	A-B	79°57½' -80°02½'	79°59½'	79°59½'
$\bar{b}$ 1126	5	C-E	58°10' -58°57'	58°37'	58°33½'

TABLE 6. PARTIAL MORPHOLOGICAL DATA, TWO-CIRCLE GONIOMETRY,
TYPE II SiC

Form	No. Times Ob- served	Quality	Observed, Weighted Averages		Calculated	
			ϕ	ρ	ϕ	ρ
$\bar{b}$ 1126	5	C-E	-0°02'*	58°32'	0°00'	58°33½'

* Zone of first order pyramids (+30°00') used as reference.

Etching experiments on a large number of type II individuals likewise proved conclusively that, although this type is hemimorphic, morphological criteria were wholly inadequate to distinguish upper from lower basal pinacoids, except in the rare case when $\bar{b}$ was present.

Although Negri's careful measurements of silicon carbide left little to be desired, axial ratios were calculated from the best observations made on type II crystals during the present investigation. These are contained in Table 7 where a comparison is afforded with the results of Negri and of Espig when the proper transformations have been made. The axial ratio retained, 4.9070, is that which gives the greatest simplification of form indices and the one indicated by x-ray studies.

Table 7 includes measurements on both green and blue black crystals. In order to ascertain whether axial ratios calculated from measurements on green SiC differed from similar calculations on the blue black, $c:a$

TABLE 7. ACCURATE MEASUREMENTS, TYPE II SiC

Form	Excellent Signals		Good Signals		Weighted Average	$c:a$	$c:a$ from Negri (1902)	$c:a$ from Espig (1921)
	Number	Average	Number	Average				
$r-\bar{r}$	5	54°46'03"	12	54°47'25"	54°46'48"	4.9070 ₄	4.9064 ₈	—
$s-\bar{s}$	24	62°06'15"	32	62°05'43"	62°06'01"	4.9069 ₆	4.9070 ₄	—
$x-\bar{x}$	11	70°33'38"	23	70°33'19"	70°33'28"	4.9068 ₈	4.9066 ₄	4.9074 ₈
$y-\bar{y}$	7	79°59'09"	24	79°59'40"	79°59'29"	4.9071 ₆	4.9074 ₄	—
				Weighted Average		4.9070	4.9069	

TABLE 8. OBSERVED AND CALCULATED AXIAL RATIOS, α -SiC TYPES

α -SiC type	Quality and Number of Observed Faces					Observed $c:a$	$c:a$ Calculated from Type II Observed Value	Per Cent Difference
	Excellent	Good	Fair	Poor	Very Poor			
II	47	91	—	—	—	4.9070	—	—
II, green	22	52	—	—	—	4.9073	4.9070	+ .006
II, blue-black	25	39	—	—	—	4.9066	4.9070	— .008
I	11	30	20	—	—	12.266 ₇	12.267 ₆	— .007
III	4	7	11	2	2	3.2713	3.2713	none
IV	1	10	10	3	0	17.189 ₇	17.174 ₆	+ .089
VI	3	22	14	6	2	26.982	26.989	— .026
I (from Negri)	(total of 428 of all qualities)					12.269 ₇	12.267 ₆	+ .018
III (from Negri)	(total of 15 of all qualities)					3.2708	3.2713	— .015

values were determined for each of these two varieties. These are included in Table 8. Although the ratios differ by seven units in the fourth decimal place, this is well within the probable limit of error for the number of angles measured and the rather high $c:a$ value.

TABLE 9. ALPHA SiC, TYPE II ANGLE TABLE

Hexagonal— P ; dihexagonal pyramidal— $6mm$.
 $a:c=1:4.9070$ $p_0:r_0=5.6661:1$

Lower	Upper		ϕ	ρ	M	A_2
$\bar{c}$	c	0001	—	0°00'	90°00'	90°00'
	m	10 $\bar{1}0$	+30°00'	90°00'	60°00'	90°00'
$\bar{n}$	n	10 $\bar{1}5$	+30°00'	48°34 $\frac{1}{2}$ '	67°59'	90°00'
$\bar{r}$	r	10 $\bar{1}4$	+30°00'	54°47'	65°53 $\frac{1}{2}$ '	90°00'
$\bar{s}$	s	10 $\bar{1}3$	+30°00'	62°06'	63°46 $\frac{1}{2}$ '	90°00'
$\bar{x}$	x	10 $\bar{1}2$	+30°00'	70°33 $\frac{1}{2}$ '	61°52'	90°00'
$\bar{y}$	y	10 $\bar{1}1$	+30°00'	79°59 $\frac{1}{2}$ '	60°30'	90°00'
$\bar{b}$		11 $\bar{2}6$	0°00'	58°33 $\frac{1}{2}$ '	90°00'	64°45'

An angle table for two-circle goniometry is given in Table 9.

Type III. The third most common form of α -SiC is designated type III. Although more numerous in previous investigations, only two crystals were found in the course of the present study. The larger, black in color, is illustrated by Fig. 3; the other, about 1 $\frac{1}{2}$ mm. in diameter, contained five faces of the form $\bar{b}$. Table 10 gives the morphological data, and Table 11 an angle table for the type. The axial ratio indicated by x -ray study yields the greatest simplification of form indices. Crystal measurement shows it to be 3.2713, which is precisely two thirds of the c value determined for type II crystals.

Type IV. Two entirely new types of hexagonal SiC were observed during the course of this study. One, represented by a single large yellow-green crystal, is designated α -SiC, type IV, and is illustrated by Fig. 4.

When this crystal was measured on the goniometer, it was immediately evident that it did not belong to any of the SiC types previously mentioned. Although, like type I, the specimen showed rhombohedral-like face development, it was characterized by an entirely different suite of trigonal pyramids only one of which was apparently equivalent to a type I form. An axial ratio was sought which would simplify the indices of the forms to the greatest extent and at the same time yield simple arithmetical series characteristic of crystals with rhombohedral lattices. When these conditions were fulfilled, the observed $c:a$ value was found to be 17.189 $_7$, a ratio which was later substantiated by x -ray study and

which, within the limits of error of the measurements, is $3\frac{1}{2}$ times that precisely determined for type II crystals.

TABLE 10. MORPHOLOGICAL DATA
TYPE III SiC

Form	No. Times Observed	Quality	Angle between Form and Base		
			Measured Range	Weight- ed Average	Calcu- lated Value
<i>c</i> 0001	1	A	—	—	0°00'
$\bar{c}$ 0001	1	A	—	—	0°00'
<i>m</i> 1010	5	A-B	89°57' -90°00 $\frac{1}{2}$ '	89°59 $\frac{1}{2}$ '	90°00'
<i>d</i> 1013	5	C-E	50°53' -51°34'	51°29'	51°32 $\frac{1}{2}$ '
<i>s</i> 1012	6	A-C	62°05' -62°08'	62°07'	62°06'
$\bar{s}$ 1012	5	A-D	62°04 $\frac{1}{2}$ ' -62°11'	62°07'	62°06'
<i>l</i> 1011	5	B-C	75°06' -75°12'	75°10'	75°10 $\frac{1}{2}$ '
$\bar{l}$ 1011	3	A-C	75°09 $\frac{1}{2}$ ' -75°11'	75°10 $\frac{1}{2}$ '	75°10 $\frac{1}{2}$ '
$\bar{b}$ 1124	5	D-E	58°32' -58°35 $\frac{1}{2}$ '	58°33'	58°33 $\frac{1}{2}$ '

TABLE 11. α -SiC, TYPE III, ANGLE TABLE

Hexagonal—*P*; dihexagonal pyramidal—6*mm*.
 $a:c = 1:3.2713$ $p_0:r_0 = 3.7774:1$

Lower	Upper		ϕ	ρ	M	A ₂
$\bar{c}$	<i>c</i>	0001	—	0°00'	90°00'	90°00'
	<i>m</i>	1010	+30°00'	90°00'	60°00'	90°00'
	<i>d</i>	1013	+30°00'	51°32 $\frac{1}{2}$ '	66°57'	90°00'
	<i>s</i>	1012	+30°00'	62°06'	63°46 $\frac{1}{2}$ '	90°00'
	<i>l</i>	1011	+30°00'	75°10 $\frac{1}{2}$ '	61°05 $\frac{1}{2}$ '	90°00'
$\bar{b}$		1124	0°00'	58°33 $\frac{1}{2}$ '	90°00'	64°45'

Table 12 gives the morphological data and Table 13 an angle table for the type.

Type V. Type V SiC is reserved for the modification with 51 formula weights per unit cell which has been reported by Ott (1928) on the basis of x-ray measurements. A morphological study of the crystal could not be made by Ott because all pyramids had been broken from the thin tabular piece. No crystal of this type was encountered during the present study, but in view of the new types IV and VI with rather high $c:a$ values and large number of formula weights per unit cell, type V is not at all improbable.

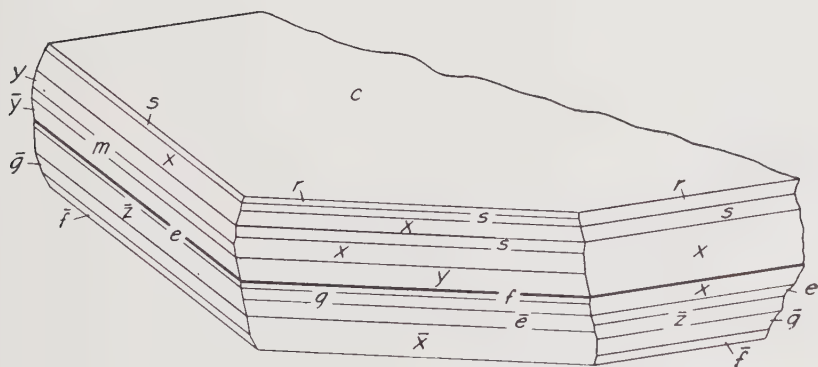
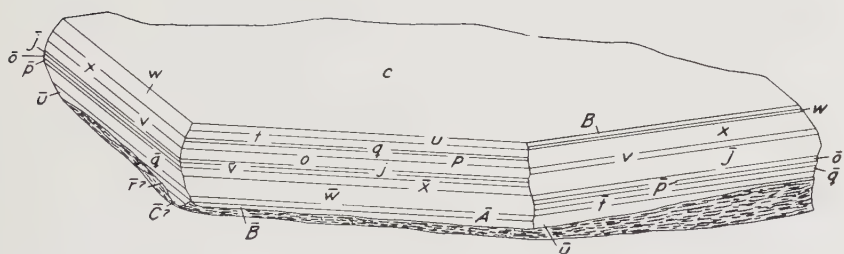
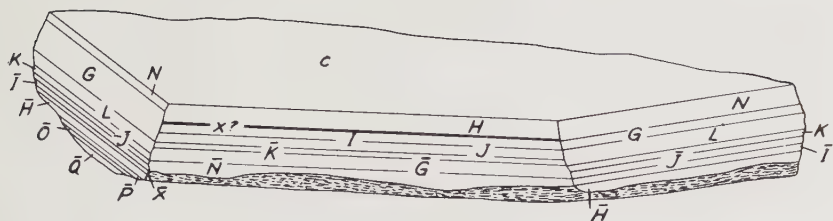


FIG. 4 (top). Alpha SiC, type IV.

FIG. 5 (center). Alpha SiC, type VI.

FIG. 6 (bottom). Coalescence of alpha SiC, type II (above), with type I (below).

TABLE 12. MORPHOLOGICAL DATA
TYPE IV SiC

Form	No. Times Ob- served	Quality	Angle between Form and Base		
			Measured Range	Weighted Average	Calcu- lated Value
c 0001	1	A	—	—	0°00'
$\bar{c}$ 0001	1	C	—	—	—
$\bar{Q}$ 0.1.1.19	1	D	46°13½'	46°13½'	46°13½'
$\bar{O}$ 0.1.1.16	1	C	51°04½'	51°04½'	51°06'
$\bar{P}$ 0.1.1.13	1	B	56°46'	56°46'	56°45'
H 1.0.1.10	1	B	63°19'	63°19'	63°14½'
$\bar{H}$ 0.1.1.10	2	C	63°03' - 63°15½'	63°09½'	
$\bar{x}$ 0117	1	C	70°41'	70°41'	70°33½'
I 1014	1	C	78°41'	78°41'	
$\bar{I}$ 0114	2	C-D	78°32' - 79°03'	78°47½'	78°36'
J 1011	1	B	87°11'	87°11'	87°07'
$\bar{J}$ 0111	2	C-D	87°16' - 87°26'	87°21'	
N 0.1.1.11	2	B	61°03' - 61°09½'	61°06½'	60°59'
$\bar{N}$ 1.0.1.11	2	B	60°54½'	60°54½'	
G 0118	2	B-C	67°59' - 68°06'	68°02½'	68°02'
$\bar{G}$ 1018	1	B	67°51½'	67°51½'	
L 0115	2	A-B	75°51½' - 75°52'	75°52'	75°51'
K 0112	2	C	83°44' - 83°57'	83°50½'	
$\bar{K}$ 1012	1	B	84°12½'	84°12½'	84°14½'

TABLE 13. α -SiC, TYPE IV, ANGLE TABLEHexagonal— R ; ditrigonal pyramidal— $3m$

$$a:c = 1:17.174_5$$

$$\alpha = 9^\circ 58'$$

$$p_0:r_0 = 19.831_4:1$$

$$\lambda = 119^\circ 45'$$

Lower	Upper		ϕ	ρ	A_1	A_2
$\bar{c}$	c	0001	—	0°00'	90°00'	90°00'
$\bar{Q}$		1.0.1.19	+30°00'	46°13½'	51°17½'	90°00'
$\bar{O}$		1.0.1.16	+30°00'	51°06'	47°37½'	90°00'
$\bar{P}$		1.0.1.13	+30°00'	56°45'	43°35½'	90°00'
$\bar{H}$	H	1.0.1.10	+30°00'	63°14½'	39°21'	90°00'
$\bar{x}$		1017	+30°00'	70°33½'	35°15'	90°00'
$\bar{I}$	I	1014	+30°00'	78°36'	31°54'	90°00'
$\bar{J}$	J	1011	+30°00'	87°07'	30°07½'	90°00'
$\bar{N}$	N	0.1.1.11	-30°00'	60°59'	90°00'	40°46½'
$\bar{G}$	G	0118	-30°00'	68°02'	90°00'	36°34'
	L	0115	-30°00'	75°51'	90°00'	32°53'
$\bar{K}$	K	0112	-30°00'	84°14½'	90°00'	30°30'

Type VI. Figure 5 illustrates a large black SiC crystal showing rhombohedral-like face development with different series of forms in alternate trigonal pyramid zones. These series, however, were entirely unlike those of any of the other α -SiC types, only the basal pinacoid and the first order pyramids r and $x\bar{x}$ being equivalent to forms found on the other types.

Again an axial ratio was sought which would offer the greatest simplification of form indices, yield simple arithmetical series of forms characteristic of crystals with rhombohedral lattices and at the same time be rationally related to the observed $c:a$ value for type II crystals. A ratio $5\frac{1}{2}$ times that of type II was found to satisfy these requirements; later the ratio was substantiated by x -ray study. Table 8 indicates that, within the limits of error of the measurements, the axial ratio is truly rationally related to that of type II.

TABLE 14. MORPHOLOGICAL DATA, TYPE VI SiC

Form	No. Times Observed	Quality	Angle between Form and Base		
			Measured Range	Weighted Average	Calculated Value
c 0001	1	A	—	—	$0^{\circ}00'$
C 1.0.1.28	2	B	$48^{\circ}00' - 48^{\circ}02\frac{1}{2}'$	$48^{\circ}01\frac{1}{2}'$	$48^{\circ}03\frac{1}{2}'$
r 1.0.1.22	2	A-B	$54^{\circ}42' - 54^{\circ}46'$	$54^{\circ}44'$	$54^{\circ}47'$
u 1.0.1.16	3	B-C	$62^{\circ}48' - 62^{\circ}51'$	$62^{\circ}49\frac{1}{2}'$	$62^{\circ}49\frac{1}{2}'$
$\bar{u}$ 0.1.1.16	2	B	$62^{\circ}45' - 62^{\circ}47\frac{1}{2}'$	$62^{\circ}46\frac{1}{2}'$	
t 1.0.1.13	2	B-D	$66^{\circ}54' - 67^{\circ}24'$	$67^{\circ}14'$	$67^{\circ}21\frac{1}{2}'$
$\bar{t}$ 0.1.1.13	1	B	$67^{\circ}24'$	$67^{\circ}24'$	
q 1.0.1.10	3	C-E	$71^{\circ}44\frac{1}{2}' - 72^{\circ}20'$	$72^{\circ}14'$	$72^{\circ}12\frac{1}{2}'$
$\bar{q}$ 0.1.1.10	2	A-B	$72^{\circ}12\frac{1}{2}' - 72^{\circ}14'$	$72^{\circ}13\frac{1}{2}'$	
p 1017	1	C	$77^{\circ}20'$	$77^{\circ}20'$	$77^{\circ}20\frac{1}{2}'$
$\bar{p}$ 0117	2	B-C	$77^{\circ}17\frac{1}{2}' - 77^{\circ}23'$	$77^{\circ}20\frac{1}{2}'$	
o 1014	1	B	$82^{\circ}43'$	$82^{\circ}43'$	$82^{\circ}41'$
$\bar{o}$ 0114	2	B	$82^{\circ}42' - 82^{\circ}44'$	$82^{\circ}43'$	
j 1011	1	B	$88^{\circ}10\frac{1}{2}'$	$88^{\circ}10\frac{1}{2}'$	$88^{\circ}09\frac{1}{2}'$
$\bar{j}$ 0111	2	A-D	$87^{\circ}47' - 88^{\circ}11'$	$88^{\circ}04'$	
D 0.1.1.26	1	B	$50^{\circ}09'$	$50^{\circ}09'$	$50^{\circ}09\frac{1}{2}'$
B 0.1.1.23	2	C-E	$53^{\circ}28\frac{1}{2}' - 53^{\circ}33'$	$53^{\circ}32'$	$53^{\circ}34\frac{1}{2}'$
$\bar{B}$ 1.0.1.23	3	C-D	$53^{\circ}38' - 53^{\circ}40\frac{1}{2}'$	$53^{\circ}39'$	
$\bar{A}$ 1.0.1.20	2	D	$57^{\circ}18\frac{1}{2}' - 57^{\circ}20\frac{1}{2}'$	$57^{\circ}19\frac{1}{2}'$	$57^{\circ}18\frac{1}{2}'$
w 0.1.1.17	3	B-C	$61^{\circ}22\frac{1}{2}' - 61^{\circ}23'$	$61^{\circ}22\frac{1}{2}'$	$61^{\circ}23'$
$\bar{w}$ 1.0.1.17	3	B-C	$61^{\circ}18\frac{1}{2}' - 61^{\circ}30\frac{1}{2}'$	$61^{\circ}24'$	
x 0.1.1.11	3	B-D	$70^{\circ}33' - 70^{\circ}37'$	$70^{\circ}34'$	$70^{\circ}33\frac{1}{2}'$
$\bar{x}$ 1.0.1.11	1	B	$70^{\circ}33\frac{1}{2}'$	$70^{\circ}33\frac{1}{2}'$	
v 0115	2	C	$80^{\circ}51\frac{1}{2}' - 80^{\circ}55\frac{1}{2}'$	$80^{\circ}53\frac{1}{2}'$	$80^{\circ}53'$
$\bar{v}$ 1015	1	C	$80^{\circ}52'$	$80^{\circ}52'$	

TABLE 15. α -SiC, TYPE VI, ANGLE TABLE

Hexagonal— R ; ditrigonal pyramidal— $3m$
 $a:c=1:26.989$ $\alpha=6^\circ 21\frac{1}{2}'$
 $p_0:r_0=31.164:1$ $\lambda=119^\circ 54'$

Lower	Upper		ϕ	ρ	A_1	A_2
	c	0001	—	$0^\circ 00'$	$90^\circ 00'$	$90^\circ 00'$
	C	$1.0.\bar{1}.28$	$+30^\circ 00'$	$48^\circ 03\frac{1}{2}'$	$49^\circ 54'$	$90^\circ 00'$
	r	$1.0.\bar{1}.22$	$+30^\circ 00'$	$54^\circ 47\frac{1}{2}'$	$44^\circ 58'$	$90^\circ 00'$
$\bar{u}$	u	$1.0.\bar{1}.16$	$+30^\circ 00'$	$62^\circ 49\frac{1}{2}'$	$39^\circ 36\frac{1}{2}'$	$90^\circ 00'$
$\bar{l}$	l	$1.0.\bar{1}.13$	$+30^\circ 00'$	$67^\circ 21\frac{1}{2}'$	$36^\circ 56\frac{1}{2}'$	$90^\circ 00'$
$\bar{q}$	q	$1.0.\bar{1}.10$	$+30^\circ 00'$	$72^\circ 12\frac{1}{2}'$	$34^\circ 27'$	$90^\circ 00'$
$\bar{p}$	p	10 $\bar{1}7$	$+30^\circ 00'$	$77^\circ 20\frac{1}{2}'$	$32^\circ 20'$	$90^\circ 00'$
$\bar{o}$	o	10 $\bar{1}4$	$+30^\circ 00'$	$82^\circ 41'$	$30^\circ 48'$	$90^\circ 00'$
$\bar{j}$	j	10 $\bar{1}1$	$+30^\circ 00'$	$88^\circ 09\frac{1}{2}'$	$30^\circ 03'$	$90^\circ 00'$
	D	$0.1.\bar{1}.26$	$-30^\circ 00'$	$50^\circ 09\frac{1}{2}'$	$90^\circ 00'$	$48^\circ 19\frac{1}{2}'$
$\bar{B}$	B	$0.1.\bar{1}.23$	$-30^\circ 00'$	$53^\circ 34\frac{1}{2}'$	$90^\circ 00'$	$45^\circ 49\frac{1}{2}'$
$\bar{A}$		$0.1.\bar{1}.20$	$-30^\circ 00'$	$57^\circ 18\frac{1}{2}'$	$90^\circ 00'$	$43^\circ 12\frac{1}{2}'$
$\bar{w}$	w	$0.1.\bar{1}.17$	$-30^\circ 00'$	$61^\circ 23'$	$90^\circ 00'$	$40^\circ 31'$
$\bar{x}$	x	$0.1.\bar{1}.11$	$-30^\circ 00'$	$70^\circ 33\frac{1}{2}'$	$90^\circ 00'$	$35^\circ 15'$
$\bar{v}$	v	01 $\bar{1}5$	$-30^\circ 00'$	$80^\circ 53'$	$90^\circ 00'$	$31^\circ 14'$

Table 14 gives the morphological data for type VI, while an angle table is included in Table 15.

Relationship of Types. It will be even more evident after the x -ray and optical data have been considered that the types are not merely different habits of hexagonal SiC, nor do they, on the other hand, represent modifications with entirely separate physical and optical properties, such as shown by the usual polymorphic substances of which calcite and aragonite may be taken as examples. In view of these relationships all the hexagonal modifications are now referred to as α -SiC, the types being designated by Roman numerals. Following Baumhauer, the phenomenon is called "polytypism" the adjective being "polytypic" and each one of the different modifications a "type." On the other hand, the cubic modification differs in crystal system and optical properties as would be expected of the usual dimorphic substances, sphalerite and wurtzite, for example, and is here designated β -SiC.

Although the axial ratios to which each of the types has been referred afford the greatest simplification of first order pyramid forms, this is not the case with the second order pyramid $\bar{b}$. If the greatest common divisor of the accepted $c:a$ ratios of the various types, 0.8178, be chosen as the axial ratio of all the modifications and Bravais indices then calculated from it, the relationships among the types and among the various forms are evident in the remarkable manner indicated in Table 16. Here

in the vertical columns are the upper forms of the various α -SiC types and the Bravais indices calculated from $c=0.8178$. This new method of notation shows that in the case of the first order pyramids the first and third or the second and third numerals of the indices are exactly the number of formula weights in the unit cells of the respective SiC types, and that the only forms which are common to two or more modifications are those forms whose indices are equivalent when referred to this greatest common divisor $c:a$ value. The table also shows that the greatest simplification of the second order pyramid is obtained by this treatment. These relationships would seem to indicate that 0.8178 is the "axial ratio" of one "molecule" of SiC which is common to all the α -SiC types.

COALESCENCE OF TYPES

The crystals thus far considered contained forms which were consistent throughout with one of the SiC types, but this was not usually the case. Figure 6 illustrates a broken but otherwise well-developed individual which actually consists of two portions; all the faces adjacent to the upper base are those of type II, while those adjacent to the lower base belong to type I. In this crystal the contact between the two types is clearly a plane which is parallel to the basal pinacoids; it is indicated on the figure by the heavy line. The outcrop of this contact on the fractured portion of the crystal is marked by a fine striation. Figure 6 thus indicates a coalescence of types I and II with common c and a axes such that the resulting mass is indistinguishable under the stereoscopic microscope from a crystal composed entirely of one type. It should be pointed out that in one zone face x is common to both types involved in the coalescence. This is possible since the form is one of those occurring in both SiC types.

Other examples found during the course of this study, in addition to the numerous cases cited by Baumhauer (1915) clearly indicate that any combination of types may coalesce in the manner described and illustrated above. It would undoubtedly be found that SiC crystals which show multitudes of small re-entrant angles and striae consist of thin plates of several of the types, or oscillations between two or more of them.

Ungemach (1935*b*) has introduced the term *syntaxie* to describe the coalescence of polytypic substances as illustrated above with the SiC types. The best English equivalent is probably "syntaxis," the adjective being "syntaxic."

In addition to this intimate and special method of contact between the various types, there are others. Crystals which are of one type throughout, for example, may appear adjacent to individuals entirely of another type, either as parallel growths or as intergrowths with no common planes, or as indicated below, twinning may involve two or more types.

TABLE 16. CORRELATION OF FORMS ON α -SiC TYPES, INDICES REFERRED TO $c:a=0.8178$
 α -SiC TYPES

I	IV	VI	II	III
c 0001	c 0001	c 0001	c 0001	c 0001
M 15.0. $\overline{15}$.13		C 33.0. $\overline{33}$.28	m 60 $\overline{60}$ (10 $\overline{10}$)	m 40 $\overline{40}$ (10 $\overline{10}$)
r 15.0. $\overline{15}$.10 (30 $\overline{32}$)	*	r 33.0. $\overline{33}$.22 (30 $\overline{32}$)	n 60 $\overline{65}$	d 40 $\overline{43}$
f 15.0. $\overline{15}$.7	N 0.21. $\overline{21}$.11	u 33.0. $\overline{33}$.16		
g 15.0. $\overline{15}$.4	G 0.21. $\overline{21}$.8	t 33.0. $\overline{33}$.13		
z 15.0. $\overline{15}$.1	L 0.21. $\overline{21}$.5	q 33.0. $\overline{33}$.10		
	K 0.21. $\overline{21}$.2	p 33.0. $\overline{33}$.7		
		o 33.0. $\overline{33}$.4		
k 0.15. $\overline{15}$.14	Q 21.0. $\overline{21}$.19	j 33.0. $\overline{33}$.1	s 60 $\overline{63}$ (20 $\overline{21}$)	s 40 $\overline{42}$ (20 $\overline{21}$)
h 0.15. $\overline{15}$.11	O 21.0. $\overline{21}$.16	D 0.33. $\overline{33}$.26		
i 0.15. $\overline{15}$.8	P 21.0. $\overline{21}$.13	B 0.33. $\overline{33}$.23		
	H 21.0. $\overline{21}$.10	A 0.33. $\overline{33}$.20		
		w 0.33. $\overline{33}$.17		
x 0.15. $\overline{15}$.5 (03 $\overline{31}$)	x 21.0. $\overline{21}$.7 (30 $\overline{31}$)	x 0.33. $\overline{33}$.11 (03 $\overline{31}$)	x 60 $\overline{62}$ (30 $\overline{31}$) = (03 $\overline{31}$)	
e 0.15. $\overline{15}$.2	I 21.0. $\overline{21}$.4 J 21.0. $\overline{21}$.1	v 0.33. $\overline{33}$.5	y 60 $\overline{61}$	l 40 $\overline{41}$
b 11 $\overline{21}$	*	*	b 11 $\overline{21}$	b 11 $\overline{21}$

* Not observed but of possible occurrence from theoretical considerations.

TWINNING

The most readily observed and probably the most frequent twinning arrangement involving α -SiC is that reported upon by previous investigators, namely, that in which the basal pinacoids of the twinned individuals are inclined to each other an average of about $70^{\circ}36'$ (obtuse angle as measured on the goniometer). The lines of contact between the individuals, which are usually tabular, are at the same time parallel to edges of the basal pinacoids of each of the portions involved in the twin. In certain areas on some lumps of crude SiC this type of twinning affects almost all of the crystals. Here repeated twinings and parallel growths are common.

In an attempt to distinguish between the two possible twinning arrangements suggested by Becke, careful determinations of the obtuse angle between the basal pinacoids were made on fifty twins of this nature chosen at random. The only twins accepted for measurement were those whose basal pinacoids adjacent to the obtuse angle afforded signals which were single and of excellent quality.

In spite of the fact that each angle is probably accurate to within $\pm 1'$, it is of particular interest to note that the observed twinning angle varied from $70^{\circ}25'$ to $70^{\circ}44'$, a range of $19'$, and that the maximum number of observations at any one angular value was 6. For comparison, the angles between the pyramids s or $\bar{s}$ and the nearest basal pinacoid of type II crystals were also measured in fifty cases at random. In spite of the lower expected accuracy of the individual readings, they varied from $62^{\circ}03'$ to $62^{\circ}08'$, or a range of only $5'$, with 26 of the angles at the one value of $62^{\circ}06'$. Eighty-eight per cent of the angles fell within $\pm 1'$ of the average, while with the case of the twins only 30% fell within this limit. These data indicate that this type of twinning in α -SiC is to be classed with parallel growths as an arrangement of individuals according to a law which is only approximately satisfied. It also explains why Becke's value for the axial ratio of SiC differs greatly from that of all other investigators (see Table 1). His value was calculated from twinning angles, while all other axial ratios were determined from interfacial angles on single crystals.

The average of the fifty observed twinning angles is $70^{\circ}35'55''$; this compares with $70^{\circ}33'10''$, the weighted average of published values on eight crystals. If the twinning satisfied the law: twinning axis perpendicular to the form r , as suggested by previous investigators, the calculated twinning angle would be $70^{\circ}26'24''$, which is lower than all but one of the fifty twins included in the study mentioned above. If the twinning plane were the possible form E (see Table 2), the calculated angle would be

$70^{\circ}37'02''$. The closer accord with the latter value might suggest this twinning law, but it is difficult to believe that the twinning is related to the complex plane E in preference to the simpler and very fundamental plane r .

In the following section on cubic SiC it will be shown that in one crystal of this substance there exist two very thin plates of α -SiC which are parallel to adjacent faces of the positive and negative tetrahedrons. These two α -SiC plates are thus inclined to one another $70^{\circ}31\frac{3}{4}'$, the octahedral angle. Since cubic SiC may be a low-temperature form which, according to Tone (1938), reverts to hexagonal SiC at an elevated temperature, it is possible that the octahedral angle might be preserved should any α -SiC twin have grown from inclusions of α -SiC in the cubic modification as described above. This possibility should be investigated experimentally before any opinion is expressed concerning the twinning law involving the individuals described above.

Eight twins were examined in detail for hexagonal SiC types involved. The most common twin of the nature described above contained individuals of type II as illustrated by Fig. 7. In one case types I and II were twinned, and in three cases individuals of type II were twinned with syntactic intergrowths of types I and II.

Another twinning arrangement was observed which involved only type I α -SiC. It is illustrated by the clinographic projection, Fig. 8, as well as by the diagram of etching figures, Fig. 10. It will be shown in the section devoted to etching that the twinning law represented here is: twinning axis, the c crystallographic axis. Although only two examples of this twinning law were encountered during the study, it is probable that it is more common in the more complex syntactic intergrowths accompanied by highly striated faces. It is also probable that the twinings described by Baumhauer and by Espig as: twinning plane parallel to the base, were in reality twinned around the c axis since these authors apparently made no experiments which were capable of distinguishing between the two possibilities. Certainly in the course of etching over a hundred α -SiC crystals during the present study nothing was observed which would indicate that the basal pinacoid was a twinning plane.

BETA SiC

Practically all samples of sized commercial silicon carbide contain less than about five per cent of particles which are either entirely isotropic, or are partially isotropic containing lamellae of anisotropic material, as is fully described in the section on optical properties.

Examination of a "pig" of SiC from the usual resistance type furnace of intermittent operation revealed a concentration of this isotropic con-

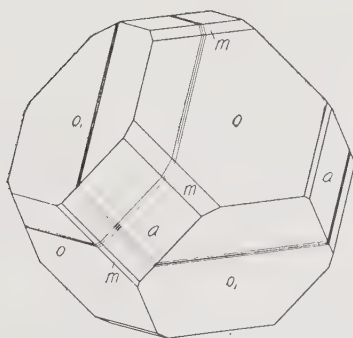
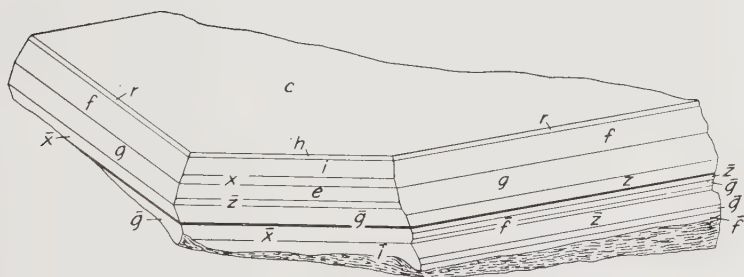
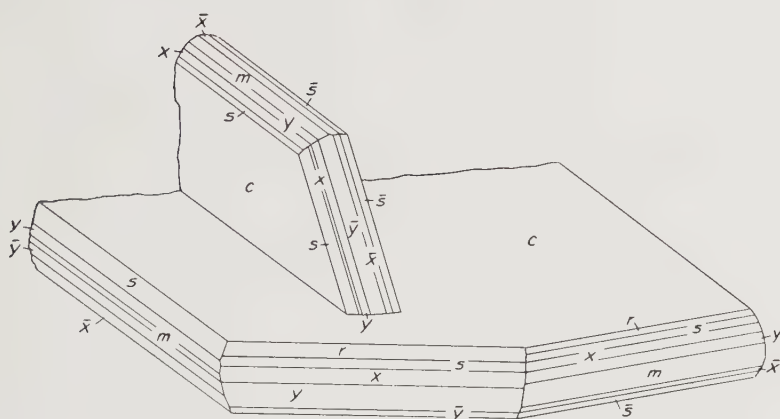


FIG. 7 (top). Most common twinning arrangement of alpha SiC. Type II twinned with type II.

FIG. 8 (center). Alpha SiC, type I, twinned with type I. Twinning axis: c crystallographic axis.

FIG. 9 (bottom). Beta (cubic) SiC. Striations indicate outcrops of included plates of alpha SiC.

stituent in the zones containing very finely crystalline SiC and "fire-sand." These occur between the area of closely intergrown larger crystals and masses of α -SiC toward the hotter core of the furnace, and the cooler zone of partially converted to unconverted material toward the outside of the "pig." Even in the fine-crystalline and "firesand" zones, however, the isotropic substance was a very minor constituent, most of the material being α -SiC with small amounts of carbon and other impurities.

Most of the isotropic substance was present as tiny irregular to rounded individuals less than $\frac{1}{2}$ mm. in size, sometimes occurring alone, but more often in the form of very finely granular aggregates showing multitudes of minute crystal faces, or associated with single or twinned crystals or aggregates of α -SiC.

Several essentially isotropic individuals were sufficiently well developed for measurement on the one-circle goniometer. One of these crystals, illustrated by Fig. 9, although only 0.27 mm. in its largest diameter, was exceptionally well developed and only slightly distorted. Transparent, olive green in color, it was practically complete and showed no apparent point of attachment to other crystals. The forms observed under the high power of a stereoscopic microscope were six faces of the cube, four each of the positive and negative tetrahedrons, and ten, possibly eleven, of a positive trigonal tristetrahedron which goniometric measurements proved to be the form $m(113)$. No faces of a corresponding negative trigonal tristetrahedron were present.

Other combinations of forms observed were: positive and negative tetrahedrons distorted by elongation parallel to one of the binary axes; a large cube face with smaller positive and negative tetrahedrons; a pseudo-hexagonal combination of cube and positive and negative tetrahedrons.

Table 17 gives the results of goniometric measurements on the four cubic crystals. Because of the extremely small size of the crystals, and hence of the faces, most of the signals were weak and broad. No signal could be obtained from some of the smallest faces although they could be seen under the high powers of a stereoscopic microscope. In spite of the poor signals obtained from these minute faces, the agreement between observed and calculated values is very satisfactory. The presence of ten, possibly eleven, faces of the positive trigonal tristetrahedron $m(113)$ with a complete absence of the corresponding negative form, and the absence of tetartohedral forms would indicate the hextetrahedral class of the isometric system.

The cubic crystal illustrated by Fig. 9, in common with most of the isotropic substance in commercial SiC, contained lamellae of anisotropic material identified as thin basal plates of α -SiC. There were two such

lamellae in this crystal. The outcrops of these on the surface of the crystal were marked by striae which are indicated on the figure. One lamella was parallel to a face of the positive tetrahedron; the second, penetrating the first, was parallel to a face of the negative tetrahedron, the two thus being inclined to each other at about $70^{\circ}32'$. It is important to

TABLE 17. MORPHOLOGICAL DATA, β -SiC

Angle	Number of Readings on Different Angles	Measured Range	Average	Calculated Value
$\alpha(001) \wedge o(111)$ or $\alpha(001) \wedge o_1(\bar{1}11)$	17	$54^{\circ}19' - 55^{\circ}13'$	$54^{\circ}45\frac{1}{4}'$	$54^{\circ}44\frac{1}{4}'$
$o(111) \wedge o_1(\bar{1}11)$	13	$70^{\circ}20' - 70^{\circ}44'$	$70^{\circ}31\frac{1}{2}'$	$70^{\circ}31\frac{3}{4}'$
$\alpha(001) \wedge m(113)$	6	$25^{\circ}00' - 25^{\circ}25'$	$25^{\circ}14\frac{1}{2}'$	$25^{\circ}14\frac{1}{4}'$
$o(111) \wedge m(113)$	7	$29^{\circ}15' - 29^{\circ}33'$	$29^{\circ}27\frac{1}{2}'$	$29^{\circ}29\frac{3}{4}'$

note that within the cubic crystal there were two tabular crystals of α -SiC intergrown in the same manner as the most common α -SiC twins and with similar inclination angle, and that the basal pinacoids of the included α -SiC plates were parallel to tetrahedron faces. The same relationships were observed on associations of the cubic substance and macroscopic crystals of α -SiC. In all cases tetrahedron faces of the cubic material were in contact with basal pinacoids of α -SiC.

Because of these facts and the additional relationships pointed out in the section on x -ray crystallography, there is little doubt that this cubic substance is an entirely different modification of SiC which will be designated β -SiC. A sufficient amount of this material could not be isolated for complete chemical analysis, but a spectroscopic analysis of a sample containing over 50% of the cubic substance, with the remainder α -SiC, was made by Dr. W. J. O'Leary and Mr. W. M. Hazel of the Norton Chippawa laboratories. A large amount of Si, a very small amount of Al and a trace of Mg were found. Because of the use of carbon electrodes the detection of this element in the sample tested was not possible.

In the relationships pointed out above, one of the four diagonal axes of trigonal symmetry in β -SiC is parallel to the c axis of α -SiC. It is not mere coincidence that both of these axes are polar, but an indication of the close structural similarity of the two modifications. The relationships also explain why α -SiC crystals twinned according to the most common law are symmetrical to a plane bisecting the acute re-entrant angle.

ETCHING FIGURES

REVIEW OF LITERATURE

Becke (1895), using a melt of NaNO_3 and Na_2CO_3 to etch SiC crystals, observed that the larger and more perfectly developed base, which he designated the upper basal pinacoid, always remained bright after etching, but contained very small six-sided etching figures having three longer sides alternating with three shorter. At the same time, the lower basal pinacoid was attacked to a greater extent and showed no etching figures. No observations concerning the results of etching on pyramid or prism faces were recorded. As a result of these observations and the evidence from crystal morphology, Becke placed SiC in the ditrigonal-pyramidal class of the hexagonal system, a determination accepted by Groth (1906). Individuals which Becke considered to be twinned on the normal to the form now designated r were symmetrical to a plane bisecting the acute re-entrant angle.

Baumhauer (1915), repeating Becke's etching experiments, was unable to obtain any clear etching figures on any of his newly discovered three types, but did observe that the basal pinacoids were differentially attacked. On a crystal of type II which he had not etched, Baumhauer observed white spots containing equilateral triangles, or two equilateral triangles one turned 60° with respect to the other. This led him to believe that type II was also ditrigonal-pyramidal.

Weigel (1916), using a melt of K_2CO_3 and KNO_3 (2:1) on a type II crystal, observed equilateral hexagons on one basal pinacoid while the other base was quite evenly dulled. Pyramids and the prism in one zone showed modified triangles which were symmetrical to a vertical plane, but which indicated the absence of a horizontal plane of symmetry. Using borax at 1000°C ., Weigel obtained equilateral hexagons on both basal pinacoids of a type II crystal and bisymmetrical rectangular etches on prism faces.

Espig (1921), using a melt of KOH , NaNO_3 and Na_2CO_3 as the etching medium, obtained a six-sided cavity with three longer sides alternating with three shorter on one base of a type I crystal and an equilateral hexagon on one base of a type II crystal. Espig referred type I to the ditrigonal-pyramidal, and type II to the dihexagonal-pyramidal class of the hexagonal system.

Although the etching experiments carried out by these investigators suggest the classes accepted by Espig, the class of type I has not been proven from these data. Moreover, Weigel's description of bisymmetrical etches on the prism of a type II crystal affords contradictory evidence for the dihexagonal-pyramidal class.

ETCHINGS BY FUSION METHODS

Because of the incomplete and inconsistent nature of the published data, a thorough study of etching was undertaken in order to determine the crystal class of each of the available SiC modifications, and the laws governing the twinning.

Crystals of types I and II were etched by all the media described in the literature. In every case, except with the use of borax, results similar to those reported by Espig were obtained, and no figures could be observed on any of the pyramids or prisms.

In order to ascertain whether, as stated by Becke, the larger and more perfectly developed base were the least attacked by a $\text{NaNO}_3\text{-Na}_2\text{CO}_3$ fusion, twelve crystals of undetermined type were selected for study. In each case one base was exceptionally large and perfectly developed, while the other base was very small and imperfect. Ten of the crystals yielded the expected result upon etching, but two were exactly opposite. Apparently Becke's generalization was based on too few observations, for it is impossible to correctly determine which is the upper and which the lower base without carefully etching each crystal, or detecting polarity by some electrical method.

Excellent etches were obtained by employing a borax fusion at red heat for a duration of 1-2 hours. Iron crucibles were used throughout this study since they were found to have sufficient life if carefully treated. Within the area defined by the dotted lines, Figure 10 shows in a diagrammatic manner the etches observed on type I α -SiC. Only mature figures of definite forms are included in the diagram which does not attempt to indicate the relative size or frequency of the etches, nor the size or shape of the crystal faces. The shape and distribution of the figures indicate three vertical planes of symmetry bisecting the first order pyramids, and a vertical axis of three-fold symmetry. The absence of a horizontal plane and center of symmetry is indicated by differential etching of the bases as well as by entirely differently shaped figures on similar pyramids at opposite ends of the crystal. .

Figure 10 shows the etching figures obtained by the use of borax on the type I twin illustrated by Fig. 8. In Figure 10, the heavy lines between certain crystal faces indicate the position of the prism which, however, does not occur in type I; the dotted line indicates the position of the composition plane of the twin. Since type I SiC has a vertical axis of three-fold symmetry and lacks a center of symmetry, the twinning law could be either: (1) twinning plane (0001), or (2) twinning axis parallel to the c crystallographic axis. Neither morphological nor x -ray study is capable of answering the question, but a study of the etching arrangement indicates that the latter is the correct twinning law.

Except that the hexagons formed on the one basal pinacoid were equilateral, the etching figures developed by fused borax on α - SiC , type II, were very similar in general appearance to those on type I. A vertical axis of six-fold symmetry and at least three vertical planes of symmetry were present, while a horizontal plane and center of symmetry were absent. The prism faces m contained etches devoid of a horizontal plane of symmetry although some of them, especially when not fully mature, were nearly the bisymmetrical rectangles reported by Weigel.

Because of the small number of type III crystals available, none was etched with borax.

Small portions chipped from α - SiC , types IV and VI, were etched by the borax method. The etching figures were very similar to those obtained on type I and the same symmetry elements are indicated.

Twenty-four examples of individuals twinned according to the most common method were etched by the Na_2CO_3 - NaNO_3 fusion method. Green and black crystals from several sources, both domestic and foreign, were included, but in all cases the twinned individuals were symmetrical to a plane bisecting the acute re-entrant angle, as observed by Becke.

ETCHINGS BY CHLORINE

Moissan (1893) stated that SiC was completely decomposed by a current of Cl_2 at about 1200°C . The substance is progressively attacked with volatilization of Si as SiCl_4 , leaving a carbon pseudomorph which may also be removed by reaction with O_2 or air at elevated temperatures forming CO_2 . It was found that a partial chlorination of suitable SiC crystals followed by a removal of the carbon by burning in air produced excellent well-defined etching figures very different in appearance from those formed by the borax fusion.

In the apparatus used for the etching, Cl_2 from the usual pressure cylinder was forced through a bubble tower partially filled with concentrated H_2SO_4 , into a fused silica tube of about one inch diameter, exit being made by rubber tubing to the outdoors. A gas-tight joint in one end of the fused silica tube permitted insertion of a fused silica boat containing the crystals to be etched. An electric furnace, cylindrical in shape with the upper half removable, entirely enclosed the central portion of the silica tube and permitted the enclosed boat with contents to reach a maximum temperature of 1000 – 1050°C ., at which temperature the etching experiments with Cl_2 were carried out. When chlorination of the crystals was judged sufficient, the Cl_2 was replaced by compressed air which removed the carbon remaining from the chlorination. In all the experiments the apparatus was operated by Mr. F. M. Fellows.

Figure 11 illustrates diagrammatically the type of etches obtained by

the Cl_2 method. In every case, whether with $\alpha\text{-SiC}$, types I, II or III, all of which were etched by this method, one basal pinacoid was very badly attacked, usually with the formation of isolated or grouped etch hillocks of modified conical shape. These were largely confined to the edges of the basal pinacoid so that when the crystal was viewed from the side, the contact between the base and the adjacent pyramid was saw-toothed as indicated in Fig. 11. The other basal pinacoid was in all cases only slightly attacked, and contained very well-defined etching figures similar to those produced by borax.

First order pyramids adjacent to the lower base contained well-defined triangles with apices pointing toward the upper base, while corresponding upper first order pyramids showed no etching figures, or, at most, tiny poorly-defined triangles with apices pointing in the same direction. Etches obtained on prism faces indicated the absence of a horizontal plane of symmetry.

Several crystals containing the second order pyramid, $\bar{b}$, were etched by the Cl_2 method, but only in the case of the type III crystal, Fig. 11, were any well-defined etches observed on these extremely minute faces. The etches observed in this case were symmetrical to a vertical plane.

Seven large crystals of types I and II were sawed in half parallel to the c axis. One-half of each crystal was etched with Cl_2 . The second half of four crystals was etched with borax, and the second half of the remaining three was etched with the $\text{Na}_2\text{CO}_3\text{-NaNO}_3$ melt. The basal pinacoid attacked to the greatest extent by the Cl_2 was also attacked most by the other etching media, and has arbitrarily been chosen the lower base in the present study.

Because of the extremely small size of all available crystals of $\beta\text{-SiC}$, no attempts were made to obtain etching figures on them.

The etching figures developed on $\alpha\text{-SiC}$, types I, IV and VI, both by fused borax and by Cl_2 at 1000°C ., admit of but one interpretation as to crystal class, namely, ditrigonal-pyramidal, or $3m$ of the hexagonal system, while types II and III are to be referred to the dihexagonal-pyramidal, or $6mm$ class of the same system.

MORPHOLOGICAL AND STRUCTURAL CRYSTALLOG- RAPHY AND OPTICAL PROPERTIES OF SILICON CARBIDE (SiC)*

PART II: STRUCTURAL CRYSTALLOGRAPHY AND OPTICAL PROPERTIES

NEWMAN W. THIBAUT,
Norton Company, Worcester, Massachusetts

TABLE OF CONTENTS

Structural Crystallography.....	328
Review of Literature.....	328
Laue Photographs.....	331
Powder Photographs.....	331
Introduction.....	331
Pattern of Each SiC Modification.....	332
Cell Dimensions and Density.....	332
Relationship of Modifications.....	343
Equi-inclination Weissenberg Photographs.....	345
Introduction.....	345
Crystal Classes.....	345
Cell Dimensions.....	345
Space Groups and Space Lattice Types.....	345
Relationship of Types.....	346
Optical Properties.....	350
Review of Literature.....	350
Alpha SiC.....	351
Examination in Polarized Light.....	351
Color and Dichroism.....	351
Indices of Refraction and Dispersion.....	354
Beta SiC.....	358
Other Polytypic Substances.....	358
References.....	360

ABSTRACT

X-ray studies were made of β -SiC and five types of α -SiC by means of powder, rotation and equi-inclination Weissenberg photographs. The following data were obtained: α -SiC, a_0 of all types when referred to smallest hexagonal cell = 3.073 Å; c_0 of all types integrally related, type I = 37.70 Å, type II = 15.07₉ Å, type III = 10.053 Å, type IV = 52.78 Å,

* Condensed from a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan, February, 1943.

type VI = 82.94 Å. Formula weights in smallest hexagonal cell = 15, 6, 4, 21, 33, respectively. Calculated density of all α -SiC types = 3.217; observed density, type II = 3.218. Space group, types I, IV, VI = C_{6v}^5-R3m ; types II and III = C_{6v}^4-C6mc . Beta SiC: $a_0 = 4.349$, formula weights in unit cell = 4, calculated density = 3.216, space group = $T_d^2-F\bar{4}3m$.

All α -SiC types are uniaxial positive. The dichroism varies considerably depending on the color, and both absorptions $\omega > \epsilon$ and $\epsilon > \omega$ were observed. The indices of refraction of all types are essentially the same, but some variation occurs within a given type: $\omega_{Na} = 2.6467-2.6487$, $\epsilon_{Na} = 2.6889-2.6930$. Dispersion (4360-6200 Å): $\omega = .0918$, $\epsilon = .1028$. Beta SiC was found to be transparent yellow to olive green, isotropic, n for red (essentially Li) light about 2.63.

The value of the study is not limited to SiC, for it may be considered the prototype of polytypic substances, many of which exist, but have not yet been studied in detail.

STRUCTURAL CRYSTALLOGRAPHY

REVIEW OF LITERATURE

Rinne (1915), (1916) published a Laue photograph of an unspecified type of SiC which was x -rayed perpendicular to the base. The presence of six-fold symmetry was said to be due to twinning, (0001) being the twinning plane.

Burdick and Owen (1918) investigated SiC of unknown type. They deduced an atomic arrangement whereby both the silicon and carbon atoms occupied face-centered rhombohedral lattices which were almost cubic, one displaced with respect to the other 0.36 of the (0001) spacing.

Hull (1919) stated that the structural arrangement of SiC was similar to that of the diamond except that half the carbon atoms, those of one of the face-centered lattices, were replaced by silicon.

Later Hull (1920) found that the powder photograph of an unknown type of SiC showed lines indicating a close-packed hexagonal structure as well as a diamond-type lattice. He concluded that there were, within the same crystal, both cubic and hexagonal close-packing of silicon atoms with carbon atoms at the centers of the tetrahedrons.

Hauer and Koller (1920) published Laue photographs perpendicular to the base of hexagonal (α) SiC, types I, II and III. Although each diagram was unique, there were many spots common to two, and a few common to all three of the SiC types. They also made a similar Laue photograph of a coalescence of types I and II. The diagram consisted of the type I pattern upon which was superposed the strongest spots of type II, equivalent spots being coincident.

Espig (1921) made Laue photographs perpendicular to (0001) and (1010) of all three of the α -SiC types. Several very thin basal sections cut from different type II crystals were x -rayed perpendicular to (0001), but all showed hexagonal symmetry, disproving the assumption of Rinne that the hexagonal pattern was due to twinning. Rotation photographs were

made of type II α -SiC using Mo radiation. The smallest cell fulfilling the wave-length requirements of the Laue photographs was said to be hexagonal with: $a_0 = 6.2 \text{ \AA}$; $c_0 = 15.3 \text{ \AA}$. It contained 24 formula weights, and the most probable space group was given as C_{60}^4 . Espig postulated the same unit cell for types I and III α -SiC but different arrangements within the cell, but no details were given.

Ott (1925*a*) gave complete structure data for type II α -SiC. The hexagonal unit cell dimensions obtained from rotation photographs using Mo radiation were: $a_0 = 3.09_5 \text{ \AA}$; $c_0 = 15.17 \text{ \AA}$. The $c_0:a_0$ ratio was thus 4.90 and the number of formula weights per cell was 6. Atomic co-ordinates were given as:

C: 0, 0, 0; 0, 0, $3/6$; $1/3$, $2/3$, $1/6$; $1/3$, $2/3$, $5/6$; $2/3$, $1/3$, $2/6$; $2/3$, $1/3$, $4/6$

Si: 0, 0, p ; 0, 0, $3/6+p$; $1/3$, $2/3$, $1/6+p$; $1/3$, $2/3$, $5/6+p$; $2/3$, $1/3$, $2/6+p$; $2/3$, $1/3$, $4/6+p$; where $p = 1/8$.

The structure was said to consist of an atom of one kind, for example C, surrounded exactly tetrahedrally by four atoms of the other kind, Si, the smallest C-Si distance being $1.9_0 \text{ \AA}$. The space group was given as C_6^6 .

Ott's second publication (1925*b*) discussed the structure of type I α -SiC. The dimensions of the smallest hexagonal cell as determined from rotation photographs were: $a_0 = 3.09_5 \text{ \AA}$, $c_0 = 37.9_5 \text{ \AA}$. The type actually was based on a rhombohedral cell containing five formula weights: $a_{rh} = 12.7_8 \text{ \AA}$ and $\alpha = 13^\circ 55'$. A possible space group was given as C_3^4 . Atomic co-ordinates in the hexagonal cell were:

C: 5 atoms at 0, 0, 0; 0, 0, $2/15$; 0, 0, $6/15$; 0, 0, $9/15$; 0, 0, $13/15$

5 atoms in similar arrangement from $-1/3$, $1/3$, $1/3$

5 atoms in similar arrangement from $1/3$, $-1/3$, $2/3$

Si: 15 atoms at the C positions $+0$, 0, p , where $p = 1/20$.

In a third paper, Ott (1926) reported on the structure of α -SiC, type III, and upon the so-called "amorphous" carbide. The unit cell of α -SiC, type III, was found to be hexagonal with $a_0 = 3.09_5 \text{ \AA}$ and $c_0 = 10.0_9 \text{ \AA}$ and to contain four formula weights. Within the limits of error of the measurements, both the c_0 value and the axial ratio were rationally related to similar values obtained for types I and II. Atomic co-ordinates of the structure were:

C: 0, 0, 0; 0, 0, $1/2$; $1/3$, $-1/3$, $1/4$; $-1/3$, $1/3$, $3/4$

Si: 0, 0, p ; 0, 0, $1/2+p$; $1/3$, $-1/3$, $1/4+p$; $-1/3$, $1/3$, $3/4+p$, where $p = 3/16$.

Gray aggregates of the "amorphous" carbide were studied by the x-ray powder diffraction method using copper radiation. They were found to be a mixture of a cubic ZnS-type substance with $a_0 = 4.37 \text{ \AA}$ —assumed to be cubic SiC—and a minor amount of α -SiC, type II.

Ott pointed out that the same exactly tetrahedral arrangement of C and Si atoms was the fundamental unit of all the SiC structures, and that the unit cells of the α -SiC types differed only in the manner in which these tetrahedrons were built up in the direction of the c -axis. The coalescence of types was readily explained since all the hexagonal modifications were similar in the plane of the a axes, the contact plane of the coalescences.

Becker (1927) gave $a_0 = 4.30 \text{ \AA}$ as the cell dimension of yellow cubic SiC.

Ott (1928) described α -SiC, type V. Rotation photographs indicated the unusual hexagonal cell: $a_0 = 3.09_5 \text{ \AA}$, $c_0 = 129.0_3 \text{ \AA}$; the type was actually based on a rhombohedral lattice with $a_{rh} = 41.1_5 \text{ \AA}$, $\alpha = 4^\circ 06'$, and contained 17 formula weights. No attempt was made to determine the atomic positions, but the relationship to the other types made it seem probable that the same tetrahedral arrangement of C and Si atoms existed here also.

Braekken (1930) examined a minute black "octahedral" crystal found in commercial SiC, and assumed to be cubic SiC. It had a ZnS-type structure with $a_0 = 4.348 \pm .005 \text{ \AA}$.

The data given by Ewald and Hermann in the *Strukturbericht I* (1931) and by Wyckoff (1931) agree with those given by Ott, except that they place α -SiC, type I, in space group C_{3v}^5 , and types II and III in group C_{6v}^4 .

Hengstenber and Garrido (1932) made a Fourier analysis showing the electron density normal to the basal pinacoid of an unspecified type of hexagonal SiC. The results were in harmony with the calculations of Ott that in the c direction carbon planes are about $2.53 \text{ \AA}$ apart and that silicon planes lie about $1.90 \text{ \AA}$ above the carbon.

Borrmann and Seyfarth (1933) gave the following data for type II SiC: $a_0 = 3.076 \pm 0.003 \text{ \AA}$; $c_0 = 15.07 \pm 0.015 \text{ \AA}$. The calculated density was 3.212 which the authors confirmed by the suspension method, although the value for the density determined in this manner was not given.

Hanawalt, Rinn and Frevel (1938) published powder photograph data for cubic and commercial SiC. The latter was said to be a mixture of cubic and hexagonal forms.

Tone (1938) stated that, in spite of the different known types of this substance, all lots of hexagonal crystals gave the same x-ray powder diffraction pattern irrespective of the source of the sample, and that lines of cubic as well as of hexagonal SiC were present in the pattern. He published a series of Laue photographs of α -SiC taken perpendicular to the base, and stated that the diagrams seemed to show a gradual transition from one type to another. No explanation was offered except that some of the differences were thought to be due to twinning.

Benner, Melton and Boyer (1940) gave $4.36_3 \text{ \AA}$ as the lattice constant of a "typical" sample of cubic SiC, and stated that the constant varied with amount of impurity to a minimum of $4.35 \text{ \AA}$. No chemical data were given.

Baumann (1941) gave x-ray powder diffraction data for SiC (type or types not stated).

LAUE PHOTOGRAPHS

If the new method of notation used in connection with the observed crystal faces for the various α -SiC types (see Table 16) is applied to the Laue photographs of Hauer and Koller (1920), the relationship between the spots of the Laue photographs of the various types is immediately evident; again only those spots are common to two or more types whose indices are equivalent when referred to the greatest common divisor $c:a$ value.

From the Laue photographs published by Hauer and Koller, Espig, and Ott, and from the observations of coalescences of α -SiC types made by Baumhauer and the writer, it seems quite certain that the Laue patterns illustrated by Tone (1938) are "transitional" because they are from crystals consisting of coalescences of types I and II in different proportions. One of his patterns is apparently influenced by a type I twin in which the c axis is the twinning axis.

The numerous satisfactory Laue photographs reproduced in the literature clearly indicate that the centro-symmetrical crystal class of α -SiC, type I, is D_{3d} , and that of types II and III is D_{6h} . Because of this and the very close morphological relationship of the new types IV and VI to the well-known type I, no Laue exposures were made during the present study.

POWDER PHOTOGRAPHS

Introduction. Because of the common occurrence of coalescences and twinning of the various α -SiC modifications, extreme care was taken in the selection of crystals of each type to be prepared for the powder photographs. Well-developed, unstriated crystals of types I, II and III were employed, while small pieces were chipped from the edges of the large basal pinacoids of types IV and VI. It was not possible to select entirely isotropic individuals of β -SiC. Instead, masses containing a minimum amount of anisotropic material were crushed for the photographs. As additional checks, at least two powder photographs were made of each of the modifications, different samples being used in each case. The fact that in all cases the different powder photographs of the same type of α -SiC were identical indicates that a desired hexagonal modification can unequivocally be selected by careful goniometric study.

All the exposures were made with filtered Cu x -radiation using a camera of about 57.3 mm. diameter, a later modification of the type described by Buerger (1936). The camera was standardized with NaCl.

Pattern of Each SiC Modification. Data from the powder photographs of each SiC modification are given in Tables 18–23 inclusive. Values are for the $\text{CuK}\alpha_1$ lines where resolved, otherwise for $\text{CuK}\alpha_1$ and α_2 . The intensity values were derived from visual comparisons of the line intensities using an arbitrary scale in which the weakest line in each photograph was numbered 1 and the strongest, 10. In the case of α -SiC the planes giving rise to the lines on the powder photographs were ascertained by correlation with those giving Weissenberg spots on the zero and first levels of a -axis rotations. The films of β -SiC were indexed by the use of the chart published by Lukesh and Chesley (1941), as well as by correlation with Weissenberg data. The calculated values of $d_{hk.l}$ for the hexagonal modifications were derived from $a_0 = 3.073 \text{ \AA}$ and the $c:a$ ratios obtained from goniometric study; those for β -SiC were based on $a_0 = 4.349 \text{ \AA}$.

Figure 12 compares the powder photographs of the various SiC modifications. A few lines, indicated by asterisks, are due to quartz from the agate mortar used for final grinding of the specimens.

Cell Dimensions and Density. Because of the discrepancies in the literature concerning the cell dimensions and the calculated and observed densities of the hexagonal SiC types, it was thought worth while to make as precise determinations of these properties as equipment and samples available would permit, and to use analyzed material.

TABLE 18. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE I

Line No.	Intensity	$hk.l$	$d_{hk.l} (\text{\AA})$	
			Observed	Calculated
1	4	$\left\{ \begin{matrix} 10.1 \\ 01.2 \end{matrix} \right\}$	2.66	$\left\{ \begin{matrix} 2.65 \\ 2.64 \end{matrix} \right\}$
2	7	10.4	2.58	2.56
3	7	$\left\{ \begin{matrix} 00.15 \\ 01.5 \end{matrix} \right\}$	2.51	$\left\{ \begin{matrix} 2.51 \\ 2.51 \end{matrix} \right\}$
4	6	10.7	2.40	2.39
5	5	01.8	2.32	2.32
6	1	10.10	2.19	2.17
7	3	01.11	2.11	2.10
8	1	10.13	1.97	1.96
9	2	01.17	1.70	1.70
10	5	10.19	1.59	1.59
11	9	$\left\{ \begin{matrix} 01.20 \\ 11.0 \end{matrix} \right\}$	1.54	$\left\{ \begin{matrix} 1.54 \\ 1.54 \end{matrix} \right\}$

TABLE 18 (Type I, *continued*)

Line No.	Intensity	$hk.l$	$d_{hk.l}$ (Å)	
			Observed	Calculated
12	5	10.22	1.444	1.441
13	4	01.23	1.398	1.396
14	2	02.4	1.320	1.318
15	8	{ 10.25 }	1.311	{ 1.312 }
		{ 11.15 }		{ 1.311 }
		{ 20.5 }		{ 1.310 }
16	2	02.7	1.297	1.292
17	2	20.8	1.281	1.281
18	2	{ 00.30 }	1.257	{ 1.257 }
		{ 02.10? }		{ 1.255 }
19	1	20.11	1.246	1.241
20	1	20.17	1.143	1.141
21	3	02.19	1.106	1.105
22	2	20.20	1.089	1.087
23	4	02.22	1.053	1.051
24	4	20.23	1.035	1.033
25	1	10.34	1.024	1.023
26	5	{ 01.35 }	1.000	{ .998 }
		{ 02.25? }		{ .998 }
		{ 21.4 }		{ 1.000 }
		{ 12.5 }		{ .997 }
27	3	21.7	.990	.989
28	3	12.8	.984	.984
29	5	{ 11.30 }	.974	{ .973 }
		{ 21.10? }		{ .972 }
30	1	12.11	.965	.965
31	4	10.37	.952	.952
32	4	01.38	.930	.930
33	1	12.17	.917	.916
34	4	21.19	.896	.897
35	7	{ 10.40 }	.888	{ .888 }
		{ 12.20 }		{ .887 }
		{ 30.0 }		{ .887 }
36	6	{ 01.41 }	.868	{ .869 }
		{ 21.22 }		{ .868 }
37	5	12.23	.858	.857
38	1	02.34	.851	.852
		{ 00.45 }		{ .838 }
39	10	{ 20.35 }	.838	{ .837 }
		{ 21.25 }		{ .837 }
		{ 20.15 }		{ .837 }
40	4	12.26	.827	.826
41	5	02.37	.809	.809
42	6	20.38	.796	.795

TABLE 19. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE II

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1	6	10.1	2.61	2.62
2	7	$\begin{Bmatrix} 00.6 \\ 10.2 \end{Bmatrix}$	2.51	$\begin{Bmatrix} 2.51 \\ 2.51 \end{Bmatrix}$
3	5	10.3	2.36	2.35
4	4	10.4	2.19	2.17
5	3	10.5	2.00	2.00
6	3	10.7	1.67	1.67
7	8	$\begin{Bmatrix} 10.8 \\ 11.0 \end{Bmatrix}$	1.54	$\begin{Bmatrix} 1.54 \\ 1.54 \end{Bmatrix}$
8	5	10.9	1.419	1.418
9	3	20.1	1.329	1.326
10	8	$\begin{Bmatrix} 10.10 \\ 11.6 \\ 20.2 \end{Bmatrix}$	1.309	$\begin{Bmatrix} 1.312 \\ 1.311 \\ 1.310 \end{Bmatrix}$
11	3	20.3	1.285	1.286
12	3	$\begin{Bmatrix} 00.12 \\ 20.4 \end{Bmatrix}$	1.253	$\begin{Bmatrix} 1.257 \\ 1.255 \end{Bmatrix}$
13	2	$\begin{Bmatrix} 10.11 \\ 20.5 \end{Bmatrix}$	1.217	$\begin{Bmatrix} 1.219 \\ 1.217 \end{Bmatrix}$
14	2	20.7	1.131	1.132
15	4	20.8	1.087	1.087
16	1	10.13	1.061	1.063
17	4	20.9	1.042	1.042
18	3	12.1	1.002	1.004
19	5	$\begin{Bmatrix} 10.14 \\ 20.10 \\ 12.2 \end{Bmatrix}$	.997	$\begin{Bmatrix} .998 \\ .998 \\ .997 \end{Bmatrix}$
20	4	12.3	.986	.986
21	5	$\begin{Bmatrix} 11.12 \\ 12.4 \end{Bmatrix}$	.972	$\begin{Bmatrix} .973 \\ .972 \end{Bmatrix}$
22	2	$\begin{Bmatrix} 20.11 \\ 12.5 \end{Bmatrix}$	.953	$\begin{Bmatrix} .955 \\ .954 \end{Bmatrix}$
23	4	10.15	.940	.940
24	3	12.7	.911	.911
25	9	$\begin{Bmatrix} 10.16 \\ 12.8 \\ 30.0 \end{Bmatrix}$	.888	$\begin{Bmatrix} .888 \\ .887 \\ .887 \end{Bmatrix}$
26	1	20.13	.873	.874
27	6	12.9	.862	.862
28	2	10.17	.841	.842
29	10	$\begin{Bmatrix} 00.18 \\ 20.14 \\ 12.10 \\ 30.6 \end{Bmatrix}$	.837	$\begin{Bmatrix} .838 \\ .837 \\ .837 \\ .837 \end{Bmatrix}$
30	3	12.11	.811	.811
31	5	20.15	.802	.802

TABLE 20. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE III

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1	4	10.0	2.67	2.66
2	5	10.1	2.59	2.57
3	4	00.4	2.52	2.51
4	5	10.2	2.36	2.35
5	3	10.3	2.08	2.08
6	2	10.4	1.83	1.83
7	4	10.5	1.61	1.60
8	6	11.0	1.54	1.54
9	5	10.6	1.419	1.418
10	7	11.4	1.311	1.311
11	4	20.2	1.287	1.286
12	3	10.7	1.264	1.264
13	2	20.3	1.238	1.237
14	2	20.4	1.178	1.176
15	1	10.8	1.136	1.136
16	4	20.5	1.111	1.110
17	5	20.6	1.042	1.042
18	3	10.9	1.030	1.030
19	4	12.1	1.000	1.001
20	5	12.2	.985	.986
21	4	$\left\{ \begin{smallmatrix} 20.7? \\ 11.8 \end{smallmatrix} \right\}$	.973	$\left\{ \begin{smallmatrix} .976 \\ .973 \end{smallmatrix} \right\}$
22	3	12.3	.963	.963
23	5	10.10	.941	.940
24	2	12.4	.933	.934
25	1	20.8	.912	.914
26	4	12.5	.899	.900
27	6	30.0	.887	.887
28	10	$\left\{ \begin{smallmatrix} 10.11 \\ 12.6 \end{smallmatrix} \right\}$	.863	$\left\{ \begin{smallmatrix} .864 \\ .862 \end{smallmatrix} \right\}$
29	3	20.9	.856	.856
30	8	$\left\{ \begin{smallmatrix} 00.12 \\ 30.4 \end{smallmatrix} \right\}$	.837	$\left\{ \begin{smallmatrix} .838 \\ .837 \end{smallmatrix} \right\}$
31	4	12.7	.824	.824
32	9	20.10	.803	.802
33	1	10.12	.798	.799
34	3	12.8	.786	.785

TABLE 21. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE IV

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1 broad	7	$\begin{Bmatrix} 01.2? \\ 10.4 \\ 01.5 \end{Bmatrix}$	2.63	$\begin{Bmatrix} 2.65 \\ 2.61 \\ 2.58 \end{Bmatrix}$
2	10	$\begin{Bmatrix} 00.21 \\ 10.7 \end{Bmatrix}$	2.53	$\begin{Bmatrix} 2.51 \\ 2.51 \end{Bmatrix}$
3	2	01.8	2.47	2.47
4	2	10.10	2.40	2.38
5	1	01.11	2.35	2.33
6	1	10.13	2.23	2.23
7	1	01.14	2.17	2.17
8 broad	3	$\begin{Bmatrix} 10.16? \\ 01.17 \end{Bmatrix}$	2.01	$\begin{Bmatrix} 2.07 \\ 2.02 \end{Bmatrix}$
9	1	10.25	1.66	1.65
10	1	01.26	1.62	1.61
11	8	$\begin{Bmatrix} 10.28 \\ 11.0 \end{Bmatrix}$	1.54	$\begin{Bmatrix} 1.54 \\ 1.54 \end{Bmatrix}$
12	2	01.29	1.51	1.50
13	3	10.31	1.442	1.434
14	2	01.32	1.407	1.402
15	1	10.34	1.337	1.341
16	7	$\begin{Bmatrix} 01.35 \\ 11.21 \\ 20.5? \\ 02.7 \\ 20.8? \end{Bmatrix}$	1.311	$\begin{Bmatrix} 1.312 \\ 1.311 \\ 1.310 \\ 1.310 \\ 1.304 \end{Bmatrix}$
17	1	02.10	1.293	1.290
18	3	$\begin{Bmatrix} 00.42 \\ 10.37 \\ 20.14? \end{Bmatrix}$	1.259	$\begin{Bmatrix} 1.257 \\ 1.257 \\ 1.255 \end{Bmatrix}$
19	1	01.38	1.229	1.231
20	1	20.26	1.114	1.113
21	2	02.28	1.089	1.087
22	2	20.29	1.076	1.074
23	2	$\begin{Bmatrix} 10.46? \\ 02.31 \end{Bmatrix}$	1.050	$\begin{Bmatrix} 1.054 \\ 1.048 \end{Bmatrix}$
24	2	$\begin{Bmatrix} 01.47? \\ 20.32 \end{Bmatrix}$	1.035	$\begin{Bmatrix} 1.035 \\ 1.036 \end{Bmatrix}$
25	5	$\begin{Bmatrix} 10.49 \\ 20.35 \\ 21.4? \\ 12.5 \\ 21.7 \\ 12.8? \end{Bmatrix}$	.999	$\begin{Bmatrix} .998 \\ .998 \\ 1.003 \\ 1.001 \\ .997 \\ .994 \end{Bmatrix}$

TABLE 21 (Type IV, *continued*)

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
26	2	$\begin{Bmatrix} 21.10 \\ 12.11^? \end{Bmatrix}$	.986	$\begin{Bmatrix} .988 \\ .984 \end{Bmatrix}$
27	4	$\begin{Bmatrix} 11.42 \\ 21.13^? \\ 12.14^? \end{Bmatrix}$	.973	$\begin{Bmatrix} .973 \\ .976 \\ .972 \end{Bmatrix}$
28	1	$\begin{Bmatrix} 20.38^? \\ 21.16^? \end{Bmatrix}$	.962	$\begin{Bmatrix} .961 \\ .962 \end{Bmatrix}$
29	2	10.52	.948	.948
30	2	01.53	.932	.933
31	1	21.25	.906	.908
32	3	$\begin{Bmatrix} 10.55 \\ 12.26 \end{Bmatrix}$	.902	$\begin{Bmatrix} .903 \\ .901 \end{Bmatrix}$
33	7	$\begin{Bmatrix} 01.56 \\ 21.28 \\ 30.0 \end{Bmatrix}$	.888	$\begin{Bmatrix} .888 \\ .887 \\ .887 \end{Bmatrix}$
34	2	12.29	.881	.880
35	3	21.31	.867	.866
36	4	$\begin{Bmatrix} 10.58^? \\ 20.47 \\ 12.32 \end{Bmatrix}$	.858	$\begin{Bmatrix} .861 \\ .858 \\ .859 \end{Bmatrix}$
37	2	21.34	.844	.844
38	9	$\begin{Bmatrix} 00.63 \\ 02.49 \\ 12.35 \\ 30.21 \end{Bmatrix}$	.837	$\begin{Bmatrix} .838 \\ .837 \\ .837 \\ .837 \end{Bmatrix}$
39	2	20.50	.828	.827
40	2	21.37	.824	.822
41	1	12.38	.815	.815
42	3	02.52	.807	.807
43	3	20.53	.797	.797
44	5	02.55	.779	.778

TABLE 22. DATA FROM X-RAY POWDER PHOTOGRAPHS OF α -SiC, TYPE VI

Line No.	Intensity	$hk.l$	$d_{hk.l}$ (Å)	
			Observed	Calculated
1 very broad	5	{ 10.4? }	2.63	{ 2.64 }
		{ 01.5 }		{ 2.63 }
		{ 10.7 }		{ 2.60 }
		{ 00.33 }		{ 2.51 }
2 broad	10	{ 10.10 }	2.53	{ 2.53 }
		{ 01.11 }		{ 2.51 }
		{ 10.16 }		{ 2.37 }
3 broad	6	{ 01.17 }	2.38	{ 2.34 }
		{ 10.22 }		{ 2.17 }
4 broad	3	{ 01.23 }	2.18	{ 2.14 }
		{ 01.26 }		{ 2.04 }
5	2	{ 10.28 }	2.00	1.98
6	2	{ 01.38 }	1.69	1.69
7	2	{ 10.40 }	1.64	1.64
8	2	{ 10.43 }	1.56	1.56
9	3	{ 01.44 }	1.54	{ 1.54 }
		{ 11.0 }		{ 1.54 }
10	8	{ 10.46 }	1.497	1.493
11	1	{ 10.49 }	1.434	1.428
12	3	{ 01.50 }	1.410	1.408
13	3	{ 10.55? }	1.313	{ 1.312 }
		{ 11.33 }		{ 1.311 }
		{ 02.10 }		{ 1.314 }
		{ 20.11 }		{ 1.310 }
14	7	{ 01.56 }	1.291	{ 1.294 }
		{ 02.16 }		{ 1.289 }
15	3	{ 00.66 }	1.260	{ 1.257 }
		{ 02.22? }		{ 1.255 }
16	3	{ 02.43 }	1.091	{ 1.095 }
		{ 20.44 }		{ 1.087 }
17 broad	2	{ 01.71? }	1.072	{ 1.070 }
		{ 02.46 }		{ 1.071 }
18	1	{ 02.49 }	1.044	{ 1.046 }
		{ 20.50 }		{ 1.038 }
		{ 01.77 }		{ .998 }
		{ 02.55 }		{ .998 }
19 broad	3	{ 12.5? }	.999	{ 1.004 }
		{ 21.7? }		{ 1.002 }
		{ 21.10 }		{ .999 }
		{ 12.11 }		{ .997 }
		{ 21.16 }		{ .987 }
20	4	{ 12.17 }	.988	{ .985 }
		{ 11.66 }		{ .973 }
21	4	{ 21.22? }	.975	{ .972 }
		{ 21.22? }		{ .972 }

TABLE 22 (Type VI, *continued*)

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
23	3	10.82	.947	.945
24	3	01.83	.936	.935
25	2	12.38	.914	.914
26	2	$\left\{ \begin{array}{l} 01.86? \\ 21.40? \end{array} \right\}$	.905	$\left\{ \begin{array}{l} .907 \\ .905 \end{array} \right\}$
27	2	21.43	.891	.892
28	5	$\left\{ \begin{array}{l} 10.88 \\ 12.44 \end{array} \right\}$	.888	$\left\{ \begin{array}{l} .888 \\ .887 \end{array} \right\}$
		30.0		.887
		01.89		.880
29	2	01.89	.880	.880
30	4	21.49	.867	.865
31	4	12.50	.860	.860
32	1	02.76	.844	.844
33	7	$\left\{ \begin{array}{l} 00.99 \\ 10.94? \end{array} \right\}$	.838	$\left\{ \begin{array}{l} .838 \\ .837 \end{array} \right\}$
		20.77		.837
		$\left\{ \begin{array}{l} 21.55? \\ 30.33 \end{array} \right\}$		$\left\{ \begin{array}{l} .837 \\ .837 \end{array} \right\}$
		02.82		.805
		20.83		.799
34	2	02.82	.806	.805
35	3	20.83	.799	.799
36	1	20.86	.781	.781

TABLE 23. DATA FROM X-RAY POWDER PHOTOGRAPHS OF BETA SiC

Line No.	Intensity	hkl	d_{hkl} (Å)	
			Observed	Calculated
1	10	111	2.51	2.51
2	1	200	2.18	2.18
3	6	220	1.54	1.54
4	6	311	1.310	1.311
5	1	222	1.256	1.255
6	2	400	1.087	1.087
7	5	331	.998	.998
8	3	420	.972	.972
9	8	422	.888	.888
10	10	$\left\{ \begin{array}{l} 333 \\ 511 \end{array} \right\}$	.837	.837

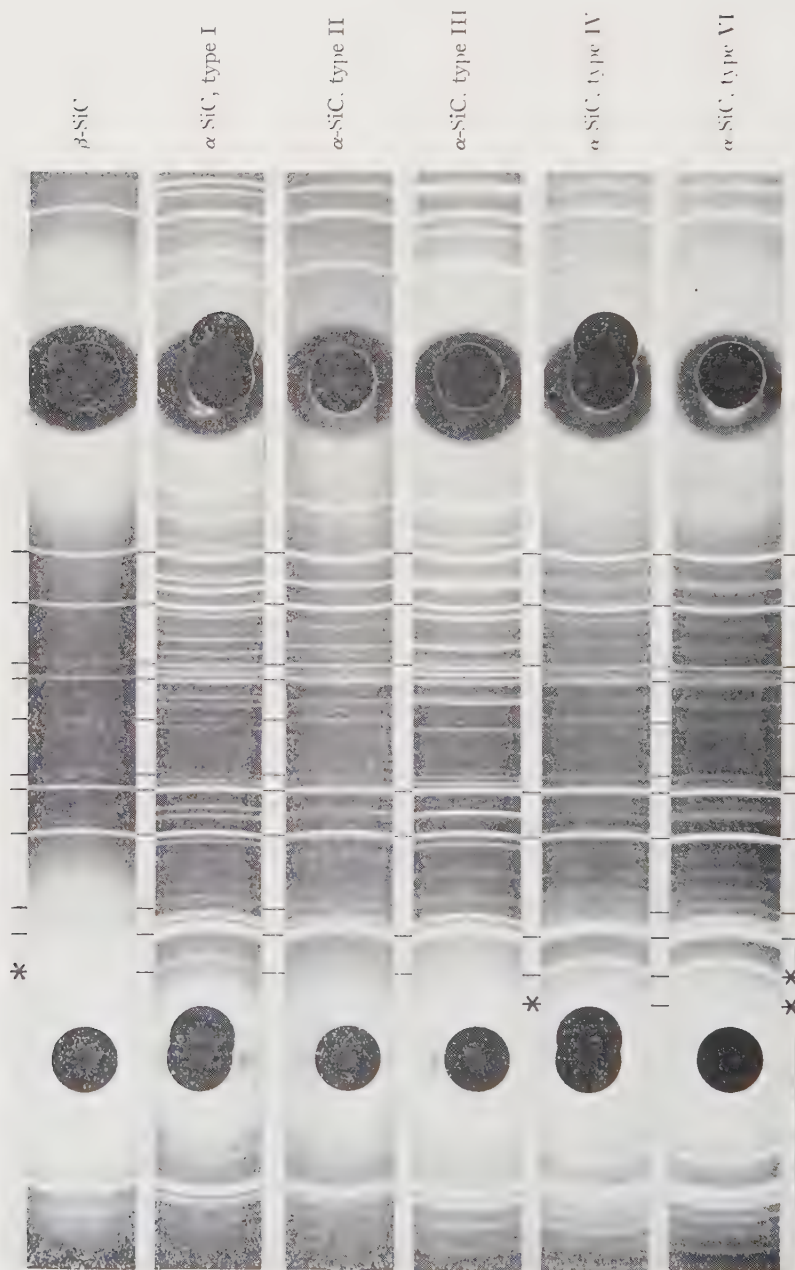


FIG. 12. X-ray Powder Photographs of the SiC Modifications. $\text{CuK}\alpha$ radiation; Camera diameter about 57.3 mm.

Accordingly, all the light green crystals of α -SiC, type II, whose crystal morphology was carefully studied and whose observed axial ratio is recorded in Table 8, were examined under a stereoscopic microscope at a magnification of 30. Those portions containing no visible impurities were segregated, crushed to -200 mesh in a steel mortar, and the magnetic portion removed. To further insure that impurities found in the analysis represented material actually within the SiC itself, either as microscopic or submicroscopic particles or in solid solution, the sample was ignited in an inclined tube furnace at 900°C. for 15 minutes in oxygen to remove any free carbon which might be present. Then it was treated with HF-HNO_3 to remove free SiO_2 , free Si, or iron introduced by powdering the sample, should these be present.

Mr. R. M. Rebert, Norton Worcester laboratories, determined the density, d at $30^{\circ}/4^{\circ}\text{C.} = 3.218$, using a 5 cc. pycnometer and xylene as the displacing liquid.

Mr. Rebert then analyzed the sample in duplicate according to the method outlined by Lamar (1939) and obtained:

		<i>Theoretical</i>
Si	69.78%	70.03%
C	29.99	29.97
Al	0.01	
Fe	0.10	
Ca	0.16	
Mg	0.01	
Total	100.05%	

From a portion of the analyzed SiC two powder photographs were prepared, one of the sample itself and another of the sample mixed with an equal portion of highest purity NaCl as a standard. The first indicated that within the limits of the method only type II was present. The second was used for a precise determination of the cell dimensions. a_0 was determined from planes 12.11 and 20.15, both of which gave well-defined doublets of medium to strong intensity in the back reflection position, and the axial ratio, 4.907, obtained from morphological study of the crystals used for the powder photograph and confirmed by equi-inclination Weissenberg photographs. The ratio, 4.907, is certainly correct to within ± 0.001 , and very likely to within ± 0.0005 . The average a_0 value calculated in this manner for type II is $3.073\text{ \AA}$ (see Table 24), and the c_0 value obtained by multiplying $a_0 \times c:a$ is $15.07_9\text{ \AA}$ (see Table 25). The calculated density is thus 3.217 which compares very favorably with the observed density of 3.218. Siegbahn's wave-lengths, 1940 International

atomic weights and the appropriate value for $1/N$, 1.6503×10^{-24} , were used in the x -ray calculations.

Similarly, from the back reflection planes of the other hexagonal SiC modifications their a_0 value was computed. The $c:a$ ratio used was the ap-

TABLE 24. CELL DIMENSION a_0 OF THE α -SiC MODIFICATIONS CALCULATED FROM THE $d_{hk.l}$ OF BACK REFLECTIONS ON POWDER PHOTOGRAPHS AND THE $c:a$ RATIO OBTAINED FROM MORPHOLOGICAL STUDY

α -SiC type	$hk.l$	$d_{hk.l}$	a_0	a_0 average
I	20.38	.7956	3.074	3.074
	02.37	.8092	3.074	
	12.26	.8271	3.075	
II	20.15	.8021	3.073	3.073
	12.11	.8106	3.072	
III	12.8	.7856	3.074	3.074
	20.10	.8025	3.075	
	12.7	.8236	3.074	
IV	02.55	.7787	3.074	3.073
	20.53	.7973	3.073	
	02.52	.8069	3.073	
VI	20.83	.7993	3.074	3.074
	02.82	.8055	3.074	

TABLE 25. CELL DIMENSIONS, FORMULA WEIGHTS PER CELL AND DENSITIES OF SiC MODIFICATIONS

Modifi- cation	Hexagonal Cell		Rhombohedral Cell		Formula Weights per Hexagonal Cell	Density	
	a_0	c_0	a_{rh}	α		Calc.	Obs.
α -SiC, I	3.073Å	37.70Å	12.69 ₁ Å	13°54 ₂ '	15	3.217	—
α -SiC, II	3.073	15.07 ₉	—	—	6	3.217	3.218
α -SiC, III	3.073	10.053	—	—	4	3.217	—
α -SiC, IV	3.073	52.78	17.68 ₃	9°58'	21	3.217	—
α -SiC, VI	3.073	82.94	27.70 ₄	6°21 ₂ '	33	3.217	—
<i>Cubic Cell</i>							
β -SiC (Cubic)	$a_0=4.349$		4			3.216	—

proprate rational multiple of 4.9070 as given in the next to the last column of Table 8 and confirmed by Weissenberg photographs. The results are indicated in Table 24. The a_0 values of all the α -SiC modifications are the same within the limits of error of the method, and 3.073 Å is retained for this dimension. The c_0 values of the other hexagonal modifications are obtained by multiplying 3.073 Å by the appropriate $c:a$ ratio, and are given in Table 25.

The cell dimension of β -SiC was determined from the average value obtained from lines 7–10 inclusive on two powder photographs of the substance. In each case, NaCl was mixed with the cubic SiC to furnish a standard. The calculated density is 3.216, remarkably close to that calculated for the hexagonal modifications.

Relationship of Modifications. It has previously been pointed out that certain planes on and within the crystals were common to two or more of the α -SiC types. Table 26 shows this relationship as derived from powder photographs. As is the case in Table 16, common planes would have the same indices if based on the greatest common divisor c_0 value; this could be obtained by dividing the “ l ” value of the indices of the α -SiC modifications of Table 26 by the number of formula weights per unit hexagonal cell for that modification.

Table 26 and Fig. 12 indicate that except for α -SiC, type III, all the hexagonal varieties contain lines which, within experimental error, are the same as those of β -SiC. This does not indicate, as many have concluded, that cubic SiC is present in the sample, but that all the planes giving powder photograph lines in β -SiC are very closely related to some of the planes of the α -SiC modifications.

The occurrence in the back reflection position of lines from equivalent planes in types II and III provided an excellent opportunity to determine whether the a_0 values of these types were the same and the c_0 values rationally related within the limits of error possible with the powder camera used, as all previous study had led the writer to conclude. A sample of the analyzed (green) type II SiC which was used for the powder photographs was intimately mixed with a sample of black type III whose powder photograph was at hand. As far as could be noted by careful examination of the film resulting from the x-raying of this mixture, all common lines were coincident and the single α_1 line due to both planes 20.10 (type III) and 20.15 (type II) was no broader than that on the photograph of either type alone. In a similar manner, other samples of the analyzed type II powder were mixed with powders of green type I, and with black type II with the same results, namely, that lines due to common planes were always strictly coincident on the photographs.

TABLE 26. X-RAY POWDER PHOTOGRAPH LINES COMMON TO THE SiC MODIFICATIONS

β -SiC <i>hkl</i>	α -SiC types				
	II	III	I	IV	VI
	<i>hk.l</i>	<i>hk.l</i>	<i>hk.l</i>	<i>hk.l</i>	<i>hk.l</i>
111	{ 00.6 10.2 10.3	00.4 — 10.2	00.15 01.5 —	00.21 10.7 —	00.33 01.11 —
200	10.4	—	10.10	01.14	10.22
220	{ 10.8 11.0 10.9	— 11.0 10.6	01.20 11.0 —	10.28 11.0 —	01.44 11.0 —
—	10.10	—	10.25	01.35	10.55?
311	{ 11.6 20.2 20.3	11.4 — 20.2	11.15 20.5 —	11.21 02.7 —	11.33 20.11 —
222	{ 00.12 20.4	— —	00.30 02.10?	00.42 20.14?	00.66 02.22?
400	20.8	—	20.20	02.28	20.44
—	20.9	20.6	—	—	—
331	{ 10.14 20.10 12.2	— — —	01.35 02.25? 12.5	10.49 20.35 21.7	01.77 02.55 12.11
—	12.3	12.2	—	—	—
420	{ 11.12 12.4	11.8 —	11.30 21.10?	11.42 12.14?	11.66 21.22?
—	10.15	10.10	—	—	—
422	{ 10.16 12.8 30.0	— — 30.0	10.40 12.20 30.0	01.56 21.28 30.0	10.88 12.44 30.0
—	12.9	12.6	—	—	—
333}	{ 00.18 20.14	00.12 —	00.45 20.35	00.63 02.49	00.99 20.77
511}	{ 12.10 30.6	— 30.4	21.25 30.15	12.35 30.21	21.55? 30.33
—	20.15	20.10	—	—	—

Tone's statement that every lot of hexagonal crystals wherever made will give the same x-ray diffraction pattern when examined by the powder method is nearly true in most cases because of the great predominance of type II in all commercial SiC. However, two different varieties of SiC manufactured commercially by the Norton Company give x-ray powder diffraction patterns which differ notably in several regions. One variety is a mixture of a large amount of type II and a small amount of type I, while

the other is predominantly type II with a smaller amount of type III.

The x -ray powder pattern of commercial SiC given by Hanawalt and co-workers (1938) and said to be of "cubic and hexagonal forms" is mainly of α -SiC type II with a small amount of type III. There was probably insufficient cubic SiC present to form any pattern. The pattern given by Baumann (1941) as characteristic for SiC contains some of the stronger lines of α -SiC, type II.

EQUI-INCLINATION WEISSENBERG PHOTOGRAPHS

Introduction. Alpha SiC, types I, II, III, IV and VI were studied with the aid of c -axis rotation photographs, and equi-inclination Weissenberg exposures of both c - and a -axis rotations, zero, first and sometimes second layer levels. In the case of β -SiC a zero level of an a -axis rotation, and zero and second layer levels of a dodecahedral axis rotation were made. Obviously not all these exposures were necessary for adequate determinations of the crystal symmetries. Exposures were made with unfiltered copper radiation. The general methods used have been described by Buerger (1942).

Because of the large c_0 cell dimensions of α -SiC, types IV and VI, and the consequent very close spacing of the layer lines of the first kind, rotation photographs were not satisfactory, and it was not always possible to screen out the first from the zero levels in c -axis rotation equi-inclination Weissenberg exposures. These difficulties were of no great consequence, however, because of the information given by a -axis Weissenberg exposures where no such ambiguities existed.

Crystal Classes. Table 27 summarizes the centro-symmetrical crystal classes indicated by plane point-group symmetries shown by the Weissenberg photographs. Actual crystal classes of α -SiC were determined by etching experiments as previously described: types I, IV and VI are C_{3v} - $3m$, and types II and III are C_{6v} - $6mm$. Morphological study of cubic SiC indicated class T_d - $\bar{4}3m$.

Cell Dimensions. The cell dimensions of all the SiC modifications were determined from the appropriate zero layer Weissenberg photographs, and aided in the precise determination of the lattice constants as discussed under the subject of powder photographs.

Space Groups and Space Lattice Types. The space groups of the various SiC modifications were obtained from characteristic absences noted on indexed Weissenberg photographs. Thus α -SiC, types I, IV and VI are C_{3v}^5 - $R3m$, since:

$(hk\bar{l})$ is present when $h-k-l=3n$

$(h \cdot h \cdot 2h \cdot l)$ is present when $l=3n$

$(hk0l)$ is present when $2h-l=3n$.

The space lattice is obviously rhombohedral as was predicted from the morphological study.

TABLE 27. CENTRO-SYMMETRICAL CRYSTAL CLASSES OF THE SiC MODIFICATIONS AS INDICATED BY PLANE POINT-GROUP SYMMETRIES OBTAINED FROM EQUI-INCLINATION WEISSENBERG PHOTOGRAPHS

SiC Modification	Rotation Axis	Level	Plane Symmetry	Centro-Symmetrical Crystal Class
α , types I, IV, VI	c [00.1]	0	C_{61}	D_{3d}
		1	C_{31}	
	a [11.0]	0	C_2	D_{3d}
		1	C_2	
α , types II, III	c [00.1]	0	C_{61}	D_{6h}
		1	C_{61}	
	a [11.0]	0	C_{21}	D_{6h}
		1	C_{21}	
β	a [100]	0	C_{41}	O_h
		0	C_{21}	O_h
	dodecahedral [110]	2	C_{21}	

The space group of α -SiC, types II and III is $C_{6v}^4 - C6mc$, since:

- (hkl) is present in all orders
- $(h \cdot h \cdot 2h \cdot l)$ is present when $l = 2n$
- (hhl) is present in all orders.

The space lattice of these types is, therefore, hexagonal as indicated by crystal morphology.

Beta-SiC is $T_d^2 - F\bar{4}3m$ from the following criteria.

- (hkl) present only when $h+k=2n$; $k+l=2n$; $l+h=2n$
- (hhl) present only when $h+l=2n$.

Relationship of Types. In Figs. 13-18 some of the common planes evident from the equi-inclination Weissenberg photographs have been indexed, and may be studied to advantage with the aid of Table 26 which shows most of the correlations to be expected.

The relationship of α -SiC and β -SiC is brought out very clearly in Fig. 18 which is an equi-inclination Weissenberg photograph of the well-developed crystal of β -SiC illustrated by Fig. 9. While this crystal was for the most part β -SiC, there were present within it two thin basal plates of α -SiC whose basal pinacoids were parallel to tetrahedral faces of the β -SiC modification. For the production of the photograph, Fig. 18, the β -SiC crystal was rotated about one of the dodecahedral axes. This was also an

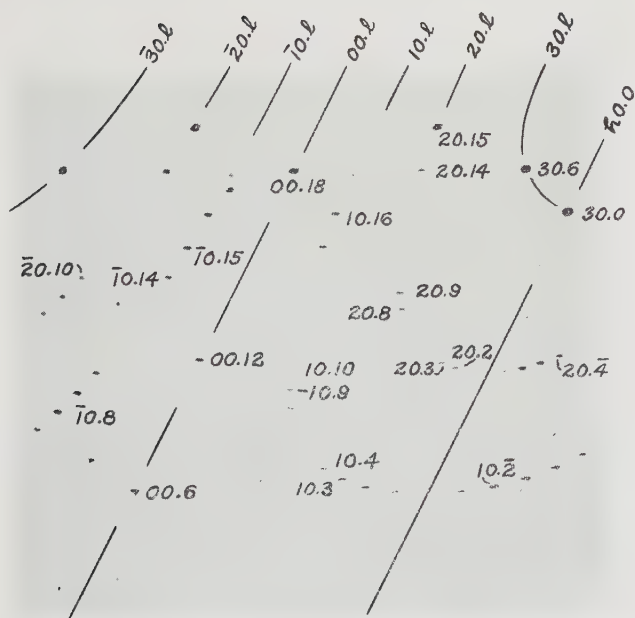
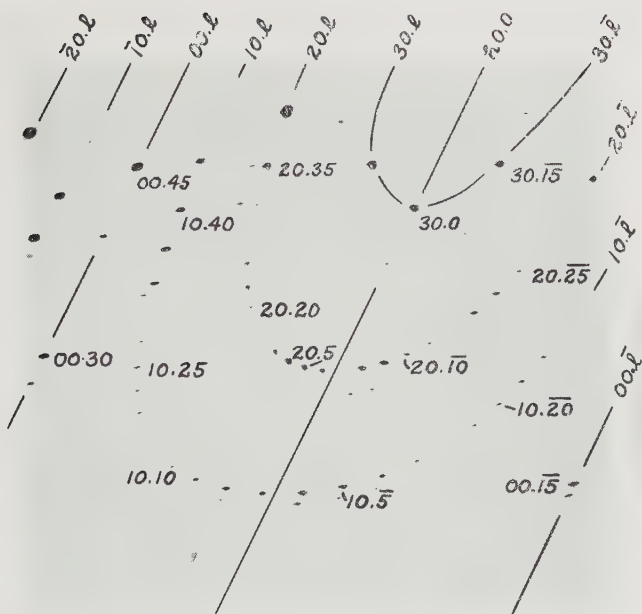


FIG. 13 (upper). Equi-inclination Weissenberg photograph of α -SiC, type I; a -axis rotation, zero level.

FIG. 14 (lower). Equi-inclination Weissenberg photograph of α -SiC, type II; a -axis rotation, zero level.

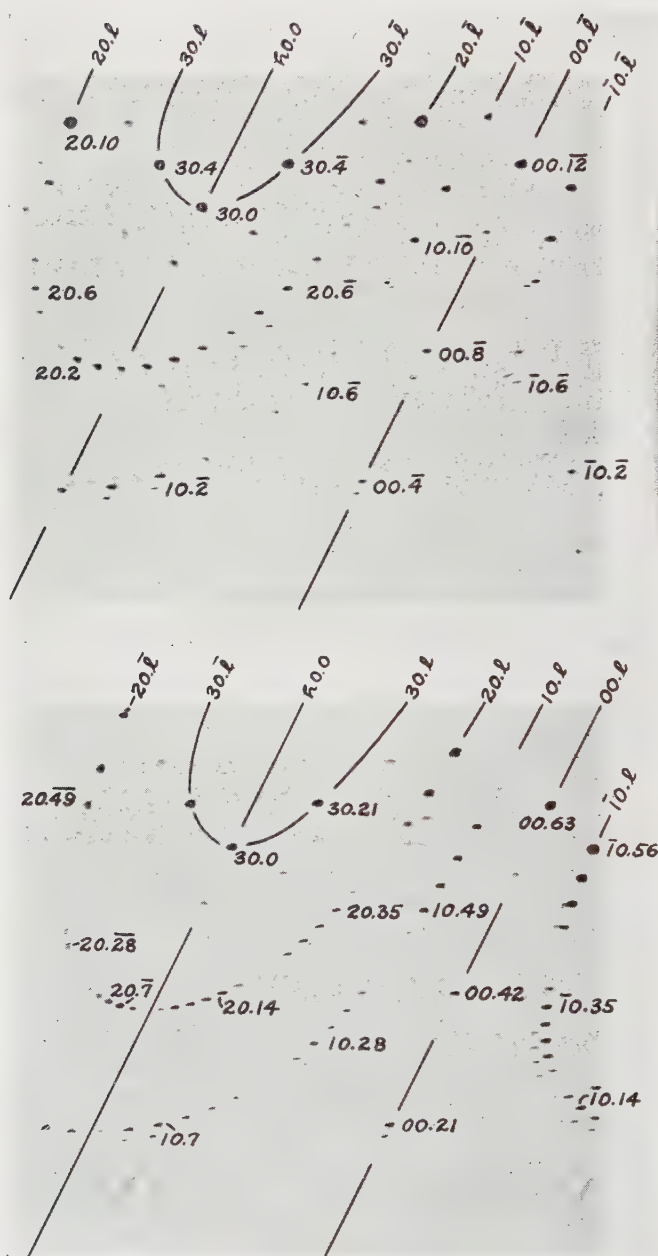


FIG. 15 (upper). Equi-inclination Weissenberg photograph of α -SiC, type III; a -axis rotation, zero level.

FIG. 16 (lower). Equi-inclination Weissenberg photograph of α -SiC, type IV; a -axis rotation, zero level.

a axis of one of the included α -SiC plates. The resulting Weissenberg photograph was essentially of β -SiC, but with additional faint spots due to an a -axis rotation of α -SiC. These faint spots are very evident on the films in the zone $00\bar{2}$ - $11\bar{1}$ -220. Comparison of this figure with Fig. 14 not only indicates that the included α -SiC plate giving the pattern was type II, but that the following points are exactly coincident.

β -SiC	α -SiC
002	10.4
11 $\bar{1}$	10.2
220	10.8

Although the determination of the ultimate structure of the SiC modifications is beyond the scope of this paper, the data concerning the existing reflections and their intensities as obtained from Weissenberg exposures of α -SiC, types I, II and III during this study are in agreement with those published by Ott. It seems quite certain that the fundamental building block of all the α -SiC modifications is one slightly distorted tetrahedron of SiC, the differences between the types being due to differences in the manner in which these are turned with respect to one another in the direction of the c -axis. All the data are likewise consistent with the sphalerite structure of β -SiC.

OPTICAL PROPERTIES

REVIEW OF LITERATURE

Frazier (1893) stated that SiC was uniaxial.

Becke (1895) obtained a uniaxial positive figure, and observed no pleochroism. The indices of refraction, determined by the Duc de Chaulnes method and measurements on interference figures, were said to be: $\omega_{Na} = 2.786$, $\epsilon_{Na} = 2.832$.

Tone (1908) published curves for the indices of refraction of SiC for various wave-lengths, the indices apparently having been calculated from interference phenomena. For sodium light the values obtained from the curves were approximately: $\omega = 2.83$, $\epsilon = 2.98$. SiC was said to be more transparent perpendicular to the c -axis than parallel to it.

Pirsson (1914) stated that SiC was uniaxial positive with weak double refraction, and that the indices for both rays were greater than 1.75. He observed some pleochroism: ϵ = deep indigo blue; ω = light blue.

Merwin (1917) determined the indices of refraction of the o ray for various wave-lengths by using the method of minimum deviation on two naturally occurring prisms found on a very pale green crystal of SiC, one face on each prism being somewhat curved. The values for the e ray were

obtained by measurements on the interference figure according to the method of Merwin (1914). The values for sodium light were: $\omega = 2.654$, $\epsilon = 2.697$. Merwin observed that bluish SiC was pleochroic light to dark blue, or olive green to greenish blue, but stated that the o ray was the more strongly absorbed.

Somewhat earlier Weigel (1916) published a paper including detailed observations on the indices of refraction of SiC for various wave-lengths and also for higher temperatures. For these purposes three prisms were very accurately ground and polished so that their refracting edges were parallel to the crystallographic c -axis. Two of the prisms were of clear, presumably light green, SiC, while the third was cut from black SiC. No determinations were made with sodium light, but interpolation gives: $\omega_{Na} = 2.6477$, $\epsilon_{Na} = 2.6934$ at about 22°C. Within experimental error, the values obtained on the black crystal were the same as those for the green crystals, so Weigel concluded that the impurity causing the color was admixed mechanically and did not exist in solid solution.

Many English-language reference texts, including Winchell (1931), Larsen and Berman (1934), and the *Handbook of Chemistry and Physics* (1943) quote Merwin's values for the indices of refraction. The *International Critical Tables* (1926) and Mellor (1924) give the values determined both by Merwin and Weigel. Winchell gives as the pleochroism formula: $X(\omega) > Z(\epsilon)$ while Larsen and Berman state: $\omega = \text{light blue}$; $\epsilon = \text{deep indigo blue}$, which would be equivalent to $Z > X$.

No optical data on cubic SiC have appeared in the literature.

ALPHA SILICON CARBIDE

Examination in Polarized Light. The normal interference figure of all the hexagonal SiC types throughout the visible spectrum is uniaxial positive. However, biaxiality due to strain, with $2V$ up to about 10° , may sometimes be observed, especially adjacent to opaque inclusions. Crystals of types I and II were examined for biaxiality but there was no evidence that it occurred more in one type than in the other.

Several pale green crystals of both types I and II up to 2 mm. in thickness were examined for optical activity in lithium, and mercury yellow, green and blue light, but there was no evidence of the rotation of the plane of polarization, nor was the interference figure that of an optically active crystal.

Color and Dichroism. Hexagonal SiC crystals are yellow, greenish-yellow, green, blue green, blue, gray, or black, the particular shade depending considerably upon the conditions of illumination, the size of the individuals and sometimes on the direction of view into the crystal. When

crushed to a fine size and observed by transmitted light, even the darkest silicon carbide will usually transmit some light and appear blue. Extremely pale green, almost colorless, crystals up to a millimeter in thickness have been found, but red SiC as reported by Winchell (1931) has not been observed by the writer. Crystals often show considerable color variation which may be irregular or zonal in nature.

The correlation between color and α -SiC type which Frazier, Baumhauer, and Espig have described was only partially substantiated. In a small sample of green crude forwarded by a foreign manufacturer there was apparently a perfect correlation between color and type, for in over 40 crystals measured from this specimen all the greenish yellow crystals were type I and all the green or blue green, type II. Moreover, when coalescences occurred, there was a sharp line of demarcation in color at the boundary between types, even when a thin plate of type I occurred between larger masses of type II. Each type was also characterized by its own dichroism as indicated by specimens 1a and 1b in Table 28.

TABLE 28. COLOR, DICHROISM AND ABSORPTION OF ALPHA SILICON CARBIDE TYPES

No.	SiC Type	Color of Crystal	Dichroism	Absorption	Remarks
1a	I	greenish yellow	ϵ =light greenish blue ω =light lemon yellow	$\epsilon > \omega?$	Coalescence of types I & II
1b	II	blue green	ϵ =medium blue green ω =light green	$\epsilon > \omega$	
2a	I	greenish yellow	ω =greenish blue ω =lemon yellow	$\epsilon > \omega?$	Different parts of same crystal, same type
2b	I	blue streak in above	ϵ =pale gray blue ω =gray blue	$\omega > \epsilon$	
3a	I	greenish yellow	ϵ =light greenish blue ω =light olive green	?	Coalescence of types I & II
3b	II	light blue	ϵ =light blue ω =very pale blue	$\epsilon > \omega$	
4a	I	green	ϵ =medium greenish blue ω =light green	$\epsilon > \omega$	Different parts of same crystal, same type
4b	I	blue streaks in above	ϵ =light gray blue ω =indigo blue	$\omega > \epsilon$	

TABLE 28—Continued

No.	SiC type	Color of Crystal	Dichroism	Absorption	Remarks
4c	II		same as 4a	$\epsilon > \omega$	4a and 4b (type I) coalesced with 4c and 4d (type II)
4d	II		same as 4b	$\omega > \epsilon$	
5	I	light yellow green	ϵ = light green ω = light buff	$\epsilon > \omega$	
6	I	blue black	ϵ = blue ω = very dark blue	$\omega > \epsilon$	
7	II	bluish green	ϵ = light blue ω = light blue green	?	
8	II	green	ϵ = blue green ω = yellow green	$\epsilon > \omega$	
9	II	light blue	ϵ = light blue ω = almost colorless	$\epsilon > \omega$	
10	II	dark blue	ϵ = light blue ω = dark blue	$\omega > \epsilon$	
11	II	black	ϵ = medium blue ω = very dark blue	$\omega > \epsilon$	From same small crude specimen
12	III	black	ϵ = medium blue ω = very dark blue	$\omega > \epsilon$	
13	IV	greenish yellow	ϵ = very pale green ω = very pale olive	$\epsilon > \omega?$	
14	VI	blue black	ϵ = medium blue ω = dark blue	$\omega > \epsilon$	
15	n.d.	blue	ϵ = pale purplish blue ω = medium blue	$\omega > \epsilon$	

A somewhat larger specimen of green SiC crude supplied by another foreign producer contained no greenish yellow or yellow crystals. Examination of over 60 crystals from this sample revealed that while most of the individuals were type II, there were a few of type I and a few coalescences. Specimens 4a, b, c, d, Table 28, are from this lot. It is to be noted

that there was no difference in color nor in dichroism between the type I and type II portions of this coalescence.

Because of the disagreement in the literature concerning the dichroism and especially the absorption formula for silicon carbide, a complete study of these properties for each of the hexagonal types was undertaken. The difficulty of obtaining satisfactory transmission of light through irregular fragments even when immersed in methylene iodide made it advisable to cut thin plates from the crystals parallel to the c axis with the aid of a suitable diamond cut-off wheel. Table 28 correlates the color, dichroism and absorption found for various crystals of the different α -SiC types.

The reason for the disagreement in the literature concerning the dichroism and absorption of hexagonal SiC no doubt is due to the variation in these properties in crystals from the same or different sources, variations which are probably caused by differences in accompanying impurities.

Indices of Refraction and Dispersion. Although the relationship between the different modifications of α -SiC clearly indicates that no differences in indices of refraction due to the structural differences between types are to be expected, it was nevertheless thought worth while to determine the indices of refraction and dispersion of two different α -SiC types. The purpose was three-fold: (1) to check the values published by Weigel and Merwin, (2) to determine experimentally whether different types were characterized by different refractive indices, and (3) to ascertain whether there were differences in indices due to material in solid solution or submicroscopic suspension in the crystal.

Prisms suitable for refractive index determinations were prepared in the following manner. A thick tabular crystal containing one large well-developed basal pinacoid was cemented to a suitable block of plate glass, the base of the crystal being in contact with the glass surface. Two cuts were then made through the crystal and into the glass with a diamond cut-off wheel such that a prism of about 40° was formed, the cut surfaces being essentially perpendicular to the basal pinacoid, and the prism edge, therefore, nearly parallel to the c -axis. For this operation the author is indebted to Dr. J. E. Burke, Norton Worcester laboratories. Each of the prism faces was polished by successively mounting in phenol formaldehyde plastic and polishing with 2 micron diamond on a lead lap, using the Graton-Vanderwilt polishing machine. The signals reflected from the prism faces on the goniometer were single, undistorted and perfectly sharp.

Three prisms were prepared in the above manner. Prism No. 1 was cut from a transparent, light green crystal of type II. It was free from flaws

and exhibited the dichroism, ϵ = medium greenish blue, ω = light green. Prism No. 2 was prepared from the same coalescence of types I and II as the plate whose dichroism is described in Table 28, specimens 1*a* and 1*b*. The purpose of cutting a prism from a coalescence was to permit a greater degree of precision in comparing the indices of refraction of the two types. If the indices of the types differed even slightly, it would be evident immediately when the minimum deviation angle was measured in monochromatic light, since four signals would be observed through the telescope of the goniometer, two from each type. This was found to be the case with prism No. 2 as is indicated by the values for the indices of refraction given in Table 29. Prism No. 3 was obtained from a green crystal of type I which varied greatly in color, and for this reason all but about one square millimeter of each prism surface was blocked off with opaque ink. The portion of prism No. 3 used to determine the indices of refraction showed the same dichroism as prism No. 1. Its identity as type I was checked by an x-ray powder photograph of the portion used for the optical examinations.

Each prism was set up on the same goniometer used for the morphological study. The prism angle was measured ten times on different parts of the scale, the average being used in the calculations. The minimum deviation angles for the ordinary and extraordinary rays through the prism were measured three times for each of the wave-lengths of light used. Finally the angle between each polished prism face and the basal pinacoid was measured five times, these measurements being necessary to determine the true ϵ value.

Omega and ϵ' were determined from the prism angles and the deviation angles by the usual formula for minimum deviation. The results appear under the columns headed " ω , 1st" and " ϵ' 1st" in Table 29. Subsequently, the prism and deviation angles were measured again, the results of these calculations appearing under the columns headed "2nd." Monochromatic light was supplied by a mercury vapor tube, hydrogen Geissler tube and sodium and lithium flames. The most precise measurements of indices of refraction given in Table 29 are indicated by asterisks. The absence of a symbol indicates average precision while less reliability is indicated by question marks. The reason for the latter was the weak signals, and therefore, somewhat uncertain deviation angles, afforded by some of the prisms for some of the wave-lengths. It is believed that the average values indicated by asterisks are correct to within ± 0.0003 .

The prisms were cut in such a manner that the refracting edges were approximately parallel to the *c*-axis. However, because of the methods employed, high precision could not be attained, and for that reason the index obtained for the extraordinary ray by the usual formula was the

TABLE 29. INDICES OF REFRACTION AND DISPERSION OF α -SiC, TYPES I AND II

Wave Length (Å)	Prism No. & SiC Type	ω			ϵ'			ϵ (calc.)
		1st	2nd	Avg.	1st	2nd	Avg.	
6708 (Li)	1, II	2.6264	2.6267	2.6266	2.6676??	2.6671??	2.6674??	2.6674??
	2a, I	—	—	—	—	—	—	—
	2b, II	—	—	—	—	—	—	—
	3, I	2.6269	2.6265	2.6267	—	—	—	—
6563 (H)	1, II	2.6294*	2.6297*	2.6296*	2.6696	2.6695	2.6696	2.6696
	2a, I	2.6283	2.6285	2.6284	—	—	—	—
	2b, II	2.6307	2.6309	2.6308	—	—	—	—
	3, I	2.6294*	2.6288*	2.6291*	2.6700?	2.6692?	2.6696?	2.6697?
5895 (Na)	1, II	2.6474*	2.6476*	2.6475*	2.6889*	2.6888*	2.6889*	2.6889*
	2a, I	2.6465	2.6469	2.6467	2.6923	2.6928	2.6926	2.6930
	2b, II	2.6485	2.6489	2.6487	2.6905	2.6904	2.6905	2.6909
	3, I	2.6470*	2.6466*	2.6468*	2.6891*	2.6890*	2.6891*	2.6892*
5781 (Hg)	1, II	2.6509*	2.6513*	2.6511*	2.6931*	2.6934*	2.6933*	2.6933*
	2a, I	2.6502*	2.6505*	2.6504*	2.6963	2.6966	2.6965	2.6969
	2b, II	2.6522*	2.6527*	2.6525*	2.6946	2.6947	2.6947	2.6951
	3, I	2.6506*	2.6505*	2.6506*	2.6930*	2.6930*	2.6930*	2.6931*
5461 (Hg)	1, II	2.6629*	2.6632*	2.6631*	2.7062*	2.7065*	2.7064*	2.7064*
	2a, I	2.6622*	2.6624*	2.6623*	2.7094	2.7096	2.7095	2.7099
	2b, II	2.6640*	2.6644*	2.6642*	2.7071	2.7073	2.7072	2.7076
	3, I	2.6625*	2.6624*	2.6625*	2.7059*	2.7065*	2.7062*	2.7063*
4867 (H)	1, II	2.6923	2.6932	2.6928	2.7410??	2.7421??	2.7416??	2.7416??
	2a, I	2.6920	2.6918	2.6919	—	—	—	—
	2b, II	2.6941	2.6945	2.6943	—	—	—	—
	3, I	2.6931	2.6923	2.6927	2.7398?	2.7409?	2.7404?	2.7405?
4358 (Hg)	1, II	2.7304	2.7305	2.7305	2.7825	2.7822	2.7824	2.7824
	2a, I	2.7298	2.7302	2.7300	2.7852?	2.7860?	2.7856?	2.7860?
	2b, II	2.7319	2.7321	2.7320	2.7835?	2.7830?	2.7833?	2.7837?
	3, I	2.7301	2.7294	2.7298	2.7818	2.7822	2.7820	2.7821
4047 (Hg)	1, II	2.7652?	2.7650?	2.7651?	—	—	—	—
	2a, I	—	—	—	—	—	—	—
	2b, II	—	—	—	—	—	—	—
	3, I	2.7635?	2.7640?	2.7638?	—	—	—	—

apparent value (ϵ') and not necessarily the true value (ϵ). The latter may be calculated from the true prism angle and the angle which each of the

prism faces makes with the basal pinacoid by the use of a series equations given by Born (1887). The writer is indebted to Mr. K. F. Whitcomb, Norton Worcester laboratories for some of the necessary calculations based on solid analytical geometry. Table 29, however, indicates that the maximum difference between ϵ' and ϵ hardly exceeds the experimental error of the best measurements of ϵ' .

Types I and II α -SiC are not characterized by different refractive indices since both ω and ϵ of prism No. 1 (type II) and prism No. 3 (type I) are the same within experimental error. From this we may conclude that the indices of refraction of all α -SiC types are fundamentally the same.

In disagreement with the conclusions of Weigel, however, differences in indices of refraction, presumably due to material in solid solution in the crystal, do occur within a single type as indicated by the differences found between the values obtained from prisms No. 1 and No. 2*b*, type II, or from prisms No. 2*a* and No. 3 both type I.

Additional proof of the influence of material in solid solution on the indices of refraction of α -SiC was afforded by prism No. 3. Although the polished prism surfaces reflected faultless signals on the goniometer, multiple signals accompanied by blurs were observed for both the ordinary and extraordinary rays passing through the prism. No indication of any biaxiality could be observed, so it seems improbable that the multiple signals were due to strains in the crystal. A marked variation in color was observed under the microscope. One area about 1 mm. square was uniformly light green, while the remainder of the prism varied from light green to medium blue. By permitting light to pass only through small portions of the prism at a time, it was found that the differently colored zones gave ordinary and extraordinary ray signals which varied slightly in position. This indicated differences in indices of refraction with color, which must be caused by variation in the amount or kind of material in solid solution or submicroscopic suspension. The indices given in Table 29 for this prism were obtained from the light green area which gave minimum values. The indices from the darker areas could not be determined satisfactorily but in some cases were certainly higher by at least 0.002.

Table 29 indicates that the following variations in indices for Na-light have been observed during the present study:

$$\omega = 2.6467\text{--}2.6487$$

$$\epsilon = 2.6889\text{--}2.6930$$

Similar variations were found for all other wave-lengths so that the dispersions of both ω and ϵ were the same for all prisms, the average values being:

$$\text{Dispersion of } \omega \text{ (4360--6200 } \text{\AA}) = 0.0918$$

$$\text{Dispersion of } \epsilon \text{ (4360--6200 } \text{\AA}) = 0.1028.$$

The data on the indices of refraction of SiC published by Becke (1895) and Tone (1908) are incorrect, since the methods used by them for the determination of the optical constants are not accurate. All of the indices of refraction determined during the course of the present study were 0.005 to 0.009 lower than the values given by Merwin for corresponding wave-lengths. This is probably due to inaccuracies resulting from the curved surfaces on Merwin's prism faces. The indices of refraction of the ordinary ray for all the prisms studied were within about 0.001 of the values given by Weigel (1916) for all wave-lengths. The ϵ of prism *2a* was within 0.0006 of Weigel's determinations for all wave-lengths, but the same values from the other prisms were 0.003 to 0.004 lower than reported by him. The dispersions agreed with the values reported by Weigel.

BETA SILICON CARBIDE

The cubic SiC encountered in the course of this study was transparent, yellow to olive green in color, and for the most part isotropic. In practically all cases, however, lamellae of an anisotropic substance were present as inclusions.

A study of β -SiC was made by embedding fragments of it in sulphur-selenium melts of known indices of refraction using fragments of a green crystal of α -SiC, type II, as control. The wave-length used was essentially equivalent to that of lithium because of the high index of the melts found necessary. The index of β -SiC for this wave-length is close to 2.63, about that of the o ray of α -SiC.

Petrographic examination of the cubic SiC crystal illustrated by Fig. 9 indicated that the anisotropic substance included within it was in the form of very thin basal plates parallel to tetrahedron faces of the β -SiC. These plates were found to be uniaxial positive with ω for Li about 2.63 and $\epsilon > 2.66$. These facts, together with similar spatial relationships found between crystals of β -SiC and macroscopic crystals of α -SiC, indicate that the lamellae are basal plates of α -SiC, confirming a conclusion already reached from x -ray studies.

OTHER POLYTYPIC SUBSTANCES

SiC was for a number of years the only known substance exhibiting the phenomenon of polytypism, and may today be considered the prototype of polytypic compounds because of the large number of types and the detail in which they have been studied. In recent years, however, data have appeared which clearly indicate that several other compounds are polytypic. For the most part the following descriptions have been taken from the literature.

Coquimbite and paracoquimbite, both with the formula $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 9\text{H}_2\text{O}$, are two minerals, which have been described as polytypic by Ungemach (1935*a*) and confirmed by Bandy (1938). The series of crystal forms of coquimbite is characteristic of a hexagonal substance while that of paracoquimbite is characteristic of a rhombohedral lattice. When the indices of the forms are simplified to the greatest extent, the indicated $c:a$ ratios are 1.5643 and 4.6928 respectively, the values being exactly rationally related as 1:3.

Rotation photographs of the two substances yielded the following cell dimensions, both being referred to the smallest hexagonal unit:

	<i>Coquimbite</i>	<i>Paracoquimbite</i>
a_0	10.8 ₅ Å	10.90 Å
c_0	17.0 ₃ Å	51.1 ₅ Å

Thus the a_0 values are probably the same, and the c_0 dimensions rationally related within the limit of error of the measurements.

Syntactic intergrowths of coquimbite and paracoquimbite are very common, several examples of which are adequately illustrated by Ungemach's crystal drawings. The plane of contact between the individuals involved in the coalescences is always the basal pinacoid, the line of demarcation often being evident on the crystal by re-entrant angles or striations.

The similarity of the morphological and structural crystallography of coquimbite and paracoquimbite to that of the α -SiC types is so evident that no comments need be made.

In a paper on syntaxis and polytypism Ungemach (1935*b*) has shown that the minerals parisite and synchisite may very reasonably be divided into three modifications or types, all having the same composition $(\text{CeF})_2\text{Ca}(\text{CO}_3)_3$. The crystals of these minerals are not as well developed as are those of SiC or coquimbite-paracoquimbite, but it seemed possible to establish the three varieties with the following $c:a$ ratios:

α -parisite (hexagonal)	= 4.473
β -parisite (rhombohedral)	= 10.094
γ -parisite (hexagonal)	= 6.730

These three axial ratios are rationally related as 4:9:6. Again certain crystal forms are common to two or all three of the varieties which often form syntactic intergrowths (coalescences).

For a number of years the x-ray powder photographs of several samples of natural graphites have been observed to show "extra" lines, apparently not due to impurities, but not indexed on the basis of the known graphite structure. Lipson and Stokes (1942*a*, 1942*b*) find that these lines may be accounted for on the assumption that there exists within these

samples about 14% of another form of graphite whose a_0 cell dimension is the same as that of ordinary graphite, but whose c_0 value is $3/2$ as great. This new structure is said to be based on a rhombohedral lattice and to belong to space group $R\bar{3}m$ whereas ordinary graphite is based on a hexagonal cell and belongs to $C6mc$. Again these appear to be polytypic compounds.

It seems quite certain that as more complete morphological and structural data concerning both minerals and artificial compounds become available, more polytypic substances will be found. The most fruitful field of search would seem to be compounds crystallizing in the hexagonal system, where polytypism might explain the appearance of two or more incompatible series of crystal forms, for example, a rhombohedral and a holohedral series, inconsistent x-ray patterns, or data seemingly showing transitions, etc. The crystal systems of lower symmetry should not be overlooked, however. The value of the optical goniometer in connection with the study of polytypic substances cannot be overemphasized, for the study of SiC has amply proven the rapidity and certainty with which the various types and the presence of syntactic intergrowths or coalescences may be determined with its aid. Entirely incorrect or inexplicable data might well result from the x-ray examination, without adequate morphological study, of a crystal which appeared to be single and well developed, but which actually was a syntactic intergrowth of two or more types.

REFERENCES

- BANDY, M. C. (1938), Mineralogy of three sulphate deposits of northern Chile: *Am. Mineral.*, **23**, 669-760.
- BAUMANN, H. N., JR. (1941), The x-ray diffraction examination of material having the composition SiC: *Trans. Electrochem. Soc.*, **80**, 95-98.
- BAUMHAUER, H. (1912), Über die Kristalle des Carborundums: *Zeits. Krist.*, **50**, 33-39.
- BAUMHAUER, H. (1915), Über die verschiedenen Modifikationen des Carborundums und die Erscheinung der Polytypie: *Zeits. Krist.*, **55**, 249-259.
- BECKE, F. (1895), Beitrag zur Kenntniss der Carborundum-krystalle CSi: *Zeits. Krist.*, **24**, 537-542.
- BECKER, K. (1927), Eine röntgenographische Methode zur Bestimmung des Wärmeausdehnungskoeffizienten bei hohen Temperaturen: *Zeits. Physik*, **40**, 37-41.
- BENNER, R. C., MELTON, R. L., AND BOYER, J. A. (1940), Silicon carbide and manufacture thereof: *Canadian Patent 393,060*, Granted December 16, 1940.
- BORN, M. (1887), Beiträge zur Bestimmung der Lichtbrechungsverhältnisse doppeltbrechender Krystalle durch Prismenbeobachtungen: *Neues Jahrb. Min., Beil.-Band V*, 1-51.
- BORRMANN, G., and SEYFARTH, H. (1933), Präzisionsbestimmung der Gitterkonstanten des Karborunds (SiC): *Zeits. Krist.*, **86**, 472-473.
- BRAEKKEN, H. (1930), Zur Kristallstruktur des kubischen Karborunds: *Zeits. Krist.*, **75**, 572-573.
- BUERGER, M. J. (1936), An x-ray powder camera: *Am. Mineral.*, **21**, 11-17.

- BUERGER, M. J. (1942), *X-ray Crystallography*. John Wiley & Son, Inc., New York.
- BURDICK, C. L., AND OWEN, E. A. (1918), The atomic structure of carborundum determined by α -rays: *Jour. Am. Chem. Soc.*, **40**, 1749-1759.
- CORTELEZZI, J., AND SCHROEDER, R. (1934), Über Carborund: *Centralb. Min., Abt. A*, **123**-128.
- ESPIG, H. (1921), Röntgenographische Untersuchungen am Karborund: *Abhand. Math.-phys. Kl. Sächs. Akad. Wiss., Leipzig*, **38**, 53-79.
- EWALD, P. P., AND HERMANN, C. (1931), Strukturbericht, 1913-1928: *Zeits. Krist., Ergänzungsband*.
- FRAZIER, B. W., AND RICHARDS, J. W. (1893), Appendix to: Acheson, E. G., Carborundum, its history, manufacture and uses: *Jour. Franklin Inst.*, **136**, 194-203; 279-289.
- GROTH, P. (1906), *Chemische Kristallographie*, Part 1, p. 56. Wilhelm Engelmann, Leipzig.
- HANAWALT, J. D., RINN, H. W., AND FREVEL, L. K. (1938), Chemical analysis by α -ray diffraction: *Ind. Eng. Chem., Anal. Ed.*, **10**, 457-512.
- HANDBOOK OF CHEMISTRY AND PHYSICS (1943), 27th edition, pp. 450, 1953. Chemical Rubber Publishing Company, Cleveland, Ohio.
- HAUER, F. V., AND KOLLER, P. (1920), Röntgenogramme von Karborundkrystallen: *Zeits. Krist.*, **55**, 260-263.
- HENGSTENBER, J., AND GARRIDO, J. (1932), Distribución electrónica en el carborundo: *Anales Soc. Españ. Fis. Quím.*, **30**, 1st part, 409-415.
- HULL, A. W. (1919), The crystal structure of carborundum: *Phys. Rev.*, **13**, 292-295.
- HULL, A. W. (1920), The crystal structure of carborundum: *Phys. Rev.*, **15**, 545-546.
- INTERNATIONAL CRITICAL TABLES (1926), First edition, vol. 7, p. 19. McGraw-Hill Book Co., Inc., New York, New York.
- LAMAR, M. O. (1939) in Furman, N. H., *Scott's Standard Methods of Chemical Analysis*, Fifth edition, vol. 1, pp. 813-816. D. Van Nostrand Co., Inc., New York, New York.
- LARSEN, E. S., AND BERMAN, H. (1934), The Microscopic Determination of the Non-opaque Minerals, 2d edition: *U. S. Geol. Surv. Bull.* **848**, 77.
- LIPSON, H., AND STOKES, A. R. (1942a), A new structure of carbon: *Nature*, **149**, 328.
- LIPSON, H., AND STOKES, A. R. (1942b), The structure of graphite: *Proc. Roy. Soc.*, **181**, 101-105.
- LUKESH, J. S., AND CHESLEY, F. G. (1941), Graphical interpretation of cubic powder patterns: *Am. Mineral.*, **26**, 395.
- MELLOR, J. W. (1924), *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, vol. 5, pp. 879-881. Longmans, Green and Co., London.
- MERWIN, H. E. (1914), Measurement of the extraordinary refractive index of a uniaxial crystal . . . : *Jour. Wash. Acad. Sci.*, **4**, 530-534.
- MERWIN, H. E. (1917), Dispersion and other optical properties of carborundum: *Jour. Wash. Acad. Sci.*, **7**, 445-447.
- MOISSAN, H. (1893), Préparation et propriétés du siliciure de carbone cristallisé: *Comptes Rendus*, **117**, 425-428.
- NEGRI, G. B. (1902), Studio cristallografico sul carborundum: *Riv. di Min. e Crist. Ital.*, **29**, 33-89; (abst.) *Zeits. Krist.*, **41**, 269-271 (1905).
- OTT, H. (1925a), Die Gitterstruktur des Karborunds (SiC) I: *Zeits. Krist.*, **61**, 515-531.
- OTT, H. (1925b), Das Gitter des Karborunds (SiC) II: *Zeits. Krist.*, **62**, 201-217.
- OTT, H. (1926), Das Gitter des Karborunds (SiC) III (III. Modifikation und das "amorphe Karbid."): *Zeits. Krist.*, **63**, 1-18.
- OTT, H. (1928), Eine neue Modifikation des Karborunds (SiC): *Festschrift "Arnold Sommerfelds"*, pp. 208-214. S. Hirzel, Leipzig.
- PEACOCK, M. A., AND SCHROEDER, R. (1934), Über die kristallographischen Elemente des Carborund: *Centralb. Min., Abt. A*, **113**-121.

- PEACOCK, M. A. (1934), Nachbemerung: *Centralb. Min., Abt. A*, 121-122.
- PIRSSON, L. V. (1914) in Dana, E. S., and Ford, W. E., *Dana's System of Mineralogy*, 6th Edition, 2d Appendix, p. 70. John Wiley and Sons, Inc., New York, N. Y.
- RINNE, F. (1915), Beiträge zur Kenntnis der Kristall-Röntgenogramme: *Ber. K. Sächs. Ges. Wiss. Leipzig, Math-phys. Kl.*, **67**, 303-340.
- RINNE, F. (1916), Beiträge zur Kenntnis des Feinbaus der Kristalle: *Neues Jahrb. Min.*, Bd. **II**, 47-108.
- TONE, F. J. (1908), Carborundum: *Min. Ind.* (during 1907), **16**, 149-156.
- TONE, F. J. (1938), The quest for hard materials: *Ind. Eng. Chem.*, **30**, 232-242.
- UNGEMACH, H. (1935a), Sur certains minéraux sulfatés du Chili: *Bull. Soc. Franç. Min.*, **58**, 97-221.
- UNGEMACH, H. (1935b), Sur la Syntaxie et la Polytypie: *Zeits. Krist.*, **91**, 1-22.
- WEIGEL, O. (1916), Über einige physikalische Eigenschaften des Carborunds: *Nach. Ges. Wiss. Gött., Math-phys. Kl.*, 264-344.
- WINCHELL, A. N. (1931), *The Microscopical Characters of Artificial Inorganic Solid Substances or Artificial Minerals*, 2d edition, p. 155. John Wiley and Sons, Inc., New York, N. Y.
- WOLFE, C. W. (1941), Crystallographic procedures: *Am. Mineral.*, **26**, 55-91.
- WYCKOFF, R. W. G. (1931), *The Structure of Crystals*, 2d Ed., pp. 222-223, 228. Chemical Catalog Co., Inc., New York, N. Y.

